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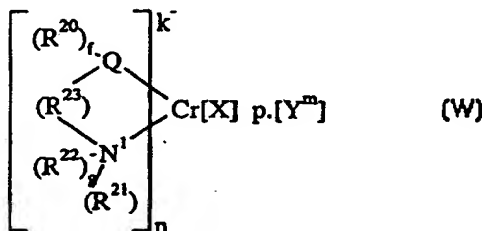
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(54) Title: NOVEL POLYMERISATION CATALYSTS



(57) Abstract

A polymerisation catalyst comprising (1) the Formula (W) compound, or dimers thereof; wherein N is nitrogen, Q is nitrogen or oxygen, X is the oxidation state of Cr and Y is an atom or a group having a valency of m, p is zero or an integer such that  $p = (X - nk)/m$  and (2) an activator compound selected from organoaluminium compounds and hydrocarbylboron compounds. The catalyst can be used for polymerising or copolymerising 1-olefins. Some novel chromium complexes are also disclosed.

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### NOVEL POLYMERISATION CATALYSTS

The present invention relates to novel polymerisation catalysts based on organic transition metal complexes and to a polymerisation process using the catalysts.

- 5           The use of certain transition metal compounds to polymerise 1-olefins, for example, ethylene, is well established in the prior art. The use of Ziegler-Natta catalysts, for example, those catalysts produced by activating titanium halides with organometallic compounds such as triethylaluminium, is fundamental to many commercial processes for manufacturing polyolefins. Over the last twenty or thirty
- 10 years, advances in the technology have led to the development of Ziegler-Natta catalysts which have such high activities that olefin polymers and copolymers containing very low concentrations of residual catalyst can be produced directly in commercial polymerisation processes. The quantities of residual catalyst remaining in the produced polymer are so small as to render unnecessary their separation and
- 15 removal for most commercial applications. Such processes can be operated by polymerising the monomers in the gas phase, or in solution or in suspension in a liquid hydrocarbon diluent. Polymerisation of the monomers can be carried out in the gas phase (the "gas phase process"), for example by fluidising under polymerisation conditions a bed comprising the target polyolefin powder and particles of the desired
- 20 catalyst using a fluidising gas stream comprising the gaseous monomer. In the so-called "solution process" the (co)polymerisation is conducted by introducing the monomer into a solution or suspension of the catalyst in a liquid hydrocarbon diluent under conditions of temperature and pressure such that the produced polyolefin forms as a solution in the hydrocarbon diluent. In the "slurry process" the temperature,
- 25 pressure and choice of diluent are such that the produced polymer forms as a suspension in the liquid hydrocarbon diluent. These processes are generally operated

at relatively low pressures (for example 10-50 bar) and low temperature (for example 50 to 150°C).

Commodity polyethylenes are commercially produced in a variety of different types and grades. Homopolymerisation of ethylene with transition metal based catalysts leads to the production of so-called "high density" grades of polyethylene. These polymers have relatively high stiffness and are useful for making articles where inherent rigidity is required. Copolymerisation of ethylene with higher 1-olefins (eg butene, hexene or octene) is employed commercially to provide a wide variety of copolymers differing in density and in other important physical properties. Particularly important copolymers made by copolymerising ethylene with higher 1-olefins using transition metal based catalysts are the copolymers having a density in the range of 0.91 to 0.93. These copolymers which are generally referred to in the art as "linear low density polyethylene" are in many respects similar to the so called "low density" polyethylene produced by the high pressure free radical catalysed polymerisation of ethylene. Such polymers and copolymers are used extensively in the manufacture of flexible blown film.

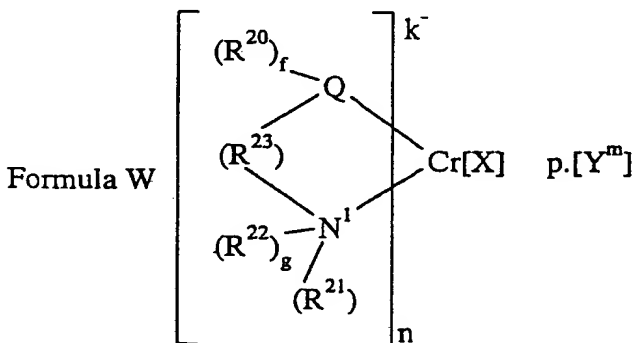
An important feature of the microstructure of the copolymers of ethylene and higher 1-olefins is the manner in which polymerised comonomer units are distributed along the "backbone" chain of polymerised ethylene units. The conventional Ziegler-Natta catalysts have tended to produce copolymers wherein the polymerised comonomer units are clumped together along the chain. To achieve especially desirable film properties from such copolymers the comonomer units in each copolymer molecule are preferably not clumped together, but are well spaced along the length of each linear polyethylene chain. In recent years the use of certain metallocene catalysts (for example biscyclopentadienylzirconiumdichloride activated with alumoxane) has provided catalysts with potentially high activity and capable of providing an improved distribution of the comonomer units. However, metallocene catalysts of this type suffer from a number of disadvantages, for example, high sensitivity to impurities when used with commercially available monomers, diluents and process gas streams, the need to use large quantities of expensive alumoxanes to achieve high activity, and difficulties in putting the catalyst on to a suitable support.

Complexes of chromium with nitrogen-containing or nitrogen and oxygen-containing organic compounds are known in the art. For example, K Folting et al in Chemical Communications, 1968, page 1170 et seq. disclose a methanol adduct of tris-(8-quinolinato)-chromium(III); RF Bryan et al in Inorganic Chemistry Vol. 10,

- No. 7 at page 1468 et seq. disclose tris(glycinato)chromium(III) monohydrate; TJ Collins et al in J. Chem. Soc., Chem. Commun., 1983 at page 681 disclose 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane of chromium(III); FE Hahn et al in J. Am. Chem. Soc., 1990 112 at page 1854 et seq. disclose diastereomeric Cr(III) and Co(III) complexes of desferri-ferrithiocin; DM Stearns et al in Inorg. Chem. 1992, 31, page 5178 et seq. disclose chromium(III)picolinate complexes; S Hao et al in Inorganica Chimica Acta.213, 1993 at page 65 et seq. disclose cyclohexylamidinate derivatives of chromium(II); and IC Chisem et al in Chem. Commun. 1998 at page 1949 et seq disclose the preparation of certain Schiff-base chromium complexes.
- However, none of these references discloses the preparation of active polymerisation catalysts based on the chromium complexes.

An object of the present invention is to provide a novel catalyst suitable for polymerising olefins, and especially for polymerising ethylene alone or for copolymerising ethylene with higher 1-olefins. A further object of the invention is to provide an improved process for the polymerisation of olefins, especially of ethylene alone or the copolymerisation of ethylene with higher 1-olefins to provide homopolymers and copolymers having controllable molecular weights. For example, using the catalyst of the present invention there can be made a wide variety of polyolefins such as, for example, liquid polyolefins, resinous or tacky polyolefins, solid polyolefins suitable for making flexible film and solid polyolefins having high stiffness.

The present invention provides a polymerisation catalyst comprising  
(1) a complex chromium compound comprising the monomeric skeletal unit depicted in Formula W, or dimers of such units;

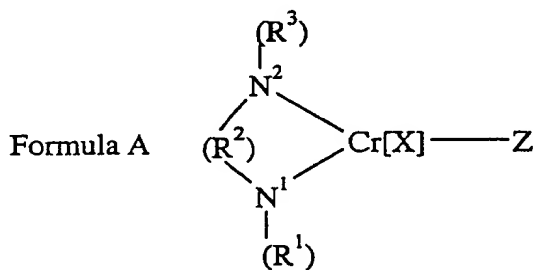


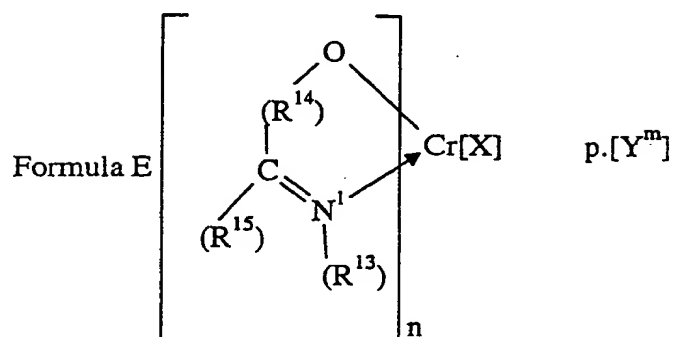
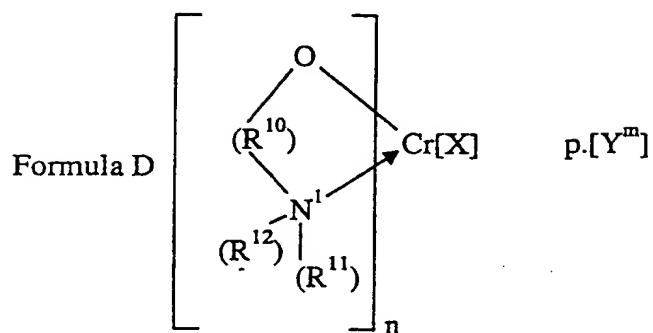
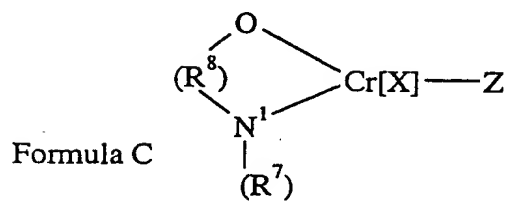
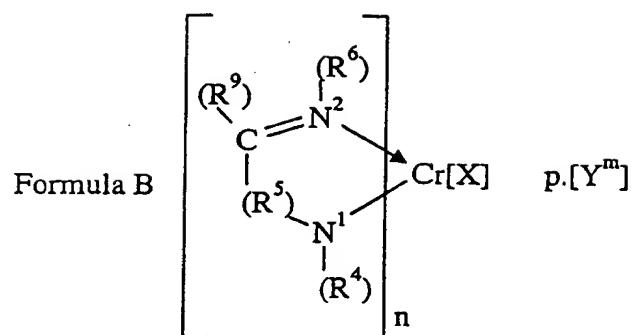
having a bidentate ligand (shown in the large square brackets) wherein  $N^1$  is a nitrogen atom, Q is a nitrogen atom  $N^2$  or an oxygen atom O,  $R^{20}$  and  $R^{21}$  are organic groups;  $R^{22}$  is hydrogen or an organic group, f and g are each independently 1 or zero provided that when f = zero Q is oxygen,  $R^{23}$  is an organic group comprising at least a saturated or unsaturated chain linking  $N^1$  with Q; two or more of  $R^{20}$ ,  $R^{21}$ ,  $R^{22}$  and  $R^{23}$  can optionally be linked to one another; the bonds between  $R^{23}$  and  $N^1$  or Q can be independently single or double bonds; and wherein k is the nominal negative charge on the bidentate ligand and is 1 or 2, n is the number of the defined bidentate ligands attached to the chromium atom and is 1 or 2, X is the oxidation state of the chromium and is 2 or 3, Y is an atom or a group having a valency of m where  $m = 1$  or 2; and p represents the number of Y atoms or groups wherein p is zero or an integer which satisfies the relationship  $p = (X - nk)/m$  and

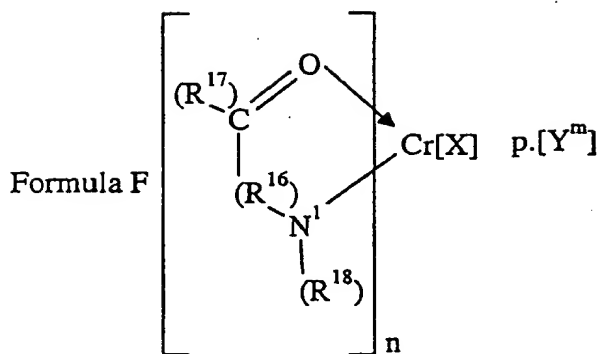
(2) an activating quantity of an activator compound selected from organoaluminium compounds and hydrocarbylboron compounds.

In addition to the defined ligand or ligands, the chromium compound can optionally comprise one or more neutral molecules coordinated to the chromium, for example, solvent molecules. Examples of such neutral molecules are ethers, amines, nitriles and esters, for example, tetrahydrofuran, acetonitrile, formdimethylamide and methyl benzoate.

In the present invention the complex chromium compound of Formula W can comprise, for example, the monomeric unit depicted in any one of Formulae A, B, C, D, E or F or dimers of such units:

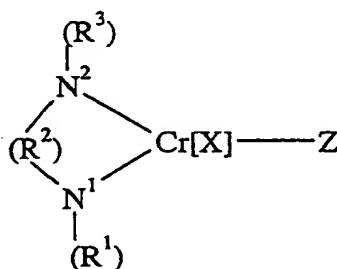






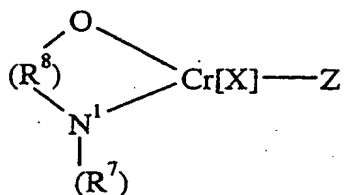
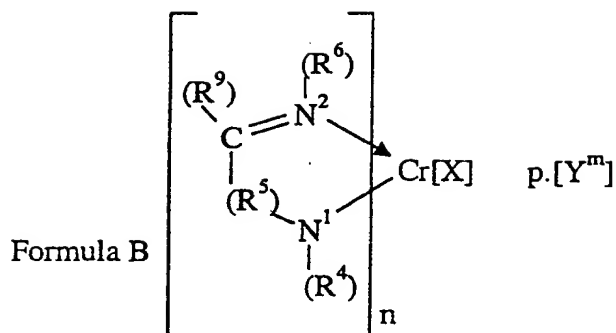
wherein  $R^2, R^5, R^8, R^{10}, R^{14}$  and  $R^{16}$  are organic groups comprising at least a saturated or unsaturated chain;  $R^1, R^3, R^4, R^6, R^7, R^{11}, R^{13}$ , and  $R^{18}$  are organic groups;  $R^9, R^{12}, R^{15}$  and  $R^{17}$  are independently hydrogen or organic groups; two or more of the defined R groups are optionally linked to one another within the respective Formula A, B, C, D, E, or F;  $N^1$  and  $N^2$  are nitrogen atoms; O is an oxygen atom; X is the oxidation state of the chromium; in Formulae A and C, X is 3; in Formula B, D, E and F, X is 2 or 3; Z is a univalent atom or group; Y is an atom or group having a valency of m, where  $m = 1$  or  $2$ ; p represents the number of atoms or groups of Y present in the complex unit; n is 1 or 2; and p is zero or an integer which satisfies the relationship  $p = (X-n)/m$ .

One embodiment of the present invention provides a polymerisation catalyst comprising (1) a complex chromium compound comprising the monomeric unit depicted in Formula A, B or C or dimers of such units:



Formula A





wherein  $\text{R}^2$ ,  $\text{R}^5$ , and  $\text{R}^8$  are organic bridging groups,  $\text{R}^1$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^6$ , and  $\text{R}^7$  are organic groups which are optionally linked to other R group(s) within the respective Formula A, B or C;  $\text{N}^1$  and  $\text{N}^2$  are nitrogen atoms; O is an oxygen atom;  $\text{R}^9$  is hydrogen or an organic group which latter is optionally linked to other R group(s) within Formula B; X is the oxidation state of the chromium; in Formulae A and C, X is 3; in Formula B, X is 2 or 3; Z is a univalent atom or group; Y is an atom or group having a valency of m, where  $m = 1$  or  $2$ ; p represents the number of atoms or groups of Y present in the complex unit; n is 1 or 2; and p is zero or an integer which satisfies the relationship  $p = (\text{X}-n)/m$  and

(2) an activating quantity of an activator compound selected from organoaluminium compounds and hydrocarbonylboron compounds.

Formulae W, A, B, C, D, E and F defined above relate to the monomeric unit of the chromium complex catalyst of the present invention. The present invention also provides catalysts comprising dimers of these units.

The defined R groups  $\text{R}^1$  to  $\text{R}^{18}$  and  $\text{R}^{20}$  to  $\text{R}^{23}$  can be, for example, an organic group selected from aliphatic, alicyclic, aromatic, carbocyclic or heterocyclic systems.

The nitrogen atoms  $\text{N}^1$  and  $\text{N}^2$  can form, for example, part of hetero-organic ring systems or hetero-organic chains. Such systems can comprise, for example,

straight or branched chain units, and can contain suitable substituents or functional groups, for example halogen, nitrile, fluoroalkyl and nitro groups.

$R^1, R^3, R^4, R^6, R^7, R^{11}, R^{13}, R^{18}, R^{20}, R^{21}$  and  $R^{22}$  can each consist of a monovalent organic group pendant from the defined nitrogen atom  $N^1$  or  $N^2$ , and can, if desired, be further bonded to one or more of the other defined R groups.  $R^9, R^{12}, R^{15}, R^{17}$  and  $R^{22}$  are independently hydrogen or organic groups and can, if desired, be further bonded to one or more of the other defined R groups.  $R^1, R^3, R^4, R^6, R^7, R^9, R^{11}, R^{12}, R^{13}, R^{15}, R^{17}, R^{18}, R^{20}, R^{21}$  and  $R^{22}$  can be independently selected from, for example, aliphatic groups, for example, methyl, ethyl, propyl, butyl, butenyl, hexyl, cyclohexyl, cyclohexenyl or octyl; or alkyaryl groups, for example, benzyl, phenylethyl or phenylpropyl; or aryl groups, for example, phenyl, naphthyl, 2,6-dimethylphenyl, 2,4-diethylphenyl, 2,6-diisopropyl or 4-chlorophenyl.

In the Formulae defined above,  $R^{23}, R^2, R^5, R^8, R^{10}, R^{14}$  and  $R^{16}$  are organic groups comprising at least a saturated or unsaturated chain linking  $N^1$  with  $N^2$  or O. In the case that the group  $R^{23}, R^2, R^5, R^8, R^{10}, R^{14}$  and  $R^{16}$  comprises a saturated chain, said chain comprises at least one carbon atom. For example, said saturated chain can have the formula  $(CR^{30}R^{31})_n$  wherein each of the substituents  $R^{30}$  and  $R^{31}$  is independently hydrogen or an organic or inorganic substituent, and n is an integer from 1 to 10, preferably from 1 to 5, most preferably from 2 to 4. Two or more of the groups  $R^{30}$  and  $R^{31}$  can be optionally linked together to form one or more ring systems. In the case that  $R^{23}, R^2, R^5, R^8, R^{10}, R^{14}$  and  $R^{16}$  comprise an unsaturated chain, said chain comprises at least two carbon atoms. The unsaturated chain preferably comprises or forms part of an aromatic ring system or a system of conjugated double bonds.

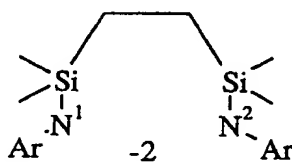
The bridging groups  $R^{23}, R^2, R^5, R^8, R^{10}, R^{14}$  and  $R^{16}$  can comprise, for example, hydrocarbyl or heterohydrocarbyl groups. They can comprise, for example, straight or branched chain aliphatic or cycloaliphatic, aromatic or heterocyclic groups. Such groups can be derived from, for example, benzene, naphthalene, phenanthrene, cyclohexane, cyclohexene, cyclopentane, pyridine, pyrimidine, quinoline, isoquinoline, acenaphthene, pyrazole, thiazole, furan, tetrahydrofuran and substituted derivatives of these types. In the case that one or more of the organic groups  $R^1$  to  $R^{23}$  are further bonded to one or more other of these organic groups within the respective Formulae A, B, C, D, E, F or W, they form ring systems including one or more of the nitrogen atoms  $N^1$  and  $N^2$ . Such ring systems may, if desired, comprise one or more

hetero atoms in addition to the one or more defined nitrogen atoms. Examples of such hetero atoms are nitrogen, silicon, sulphur and oxygen.

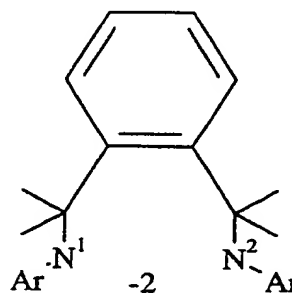
The ring systems can include, for example, straight or branched chain hydrocarbon or heterohydrocarbonyl units. Further ring systems can be fused thereto, for example, units derived from benzene, naphthalene, phenanthrene, cyclohexane, cyclohexene, cyclopentane, pyridine, pyrimidine, quinoline, isoquinoline, acenaphthene, pyrazole, thiazole, furan, tetrahydrofuran and substituted derivatives thereof. The ring systems can contain suitable substituents or functional groups, for example halogen, nitrile, fluoroalkyl and nitro groups.

The following are examples of bidentate ligands which can be the ligands present in the chromium complex catalysts of the present invention:

1. Ligands of the Formula A type:

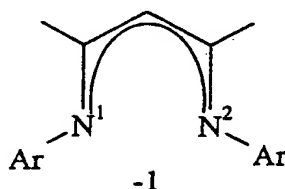


Ligand A7 - Diamide

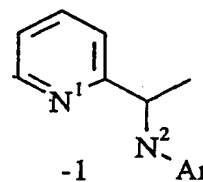


Ligand A8 - Diamide

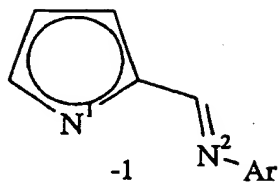
2. Ligands of the Formula B type:



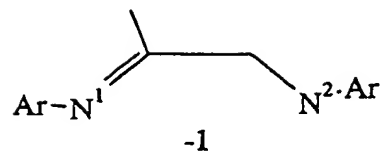
Ligand B11 -  
Beta-diketimate



Ligand B12 -  
Pyridyl-amide

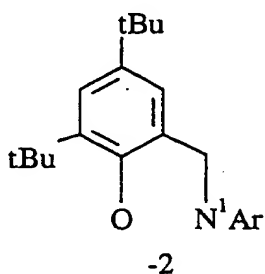


Ligand B13 -  
Pyrrolide-imine



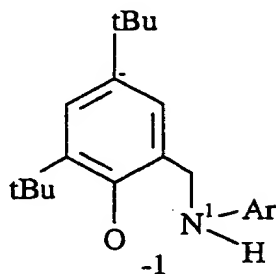
Ligand B14 -  
Imine-amide

3. Ligands of the Formula C type:



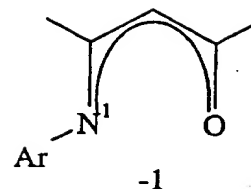
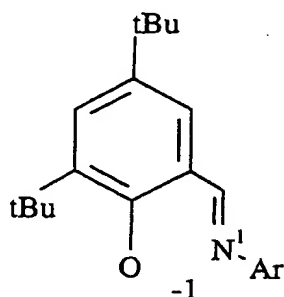
Ligand C3 -  
Alkoxide-amide

4. Ligands of the Formula D type:



Ligand D1 -  
Alkoxide-amine

5. Ligands of the Formula E type:

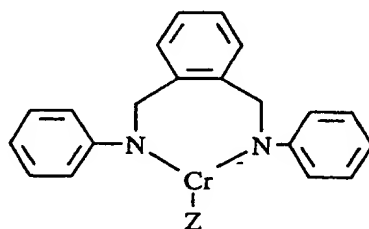


Lignand E1 -  
Alkoxide-Imine

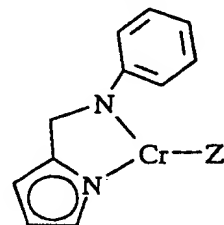
Ligand E2 -  
Beta-keeton-ketim-ate

The following Formulae are provided as illustrative examples of chromium complexes suitably comprised by the catalyst of the present invention. Formulae A1, A2 and A3 illustrate units of the Formula A type, Formulae B1, B2, B3 and B4 illustrate Formula B type and Formula C1 illustrates a unit of the Formula C type. Illustrations of Formula D and E types are shown later in this specification.

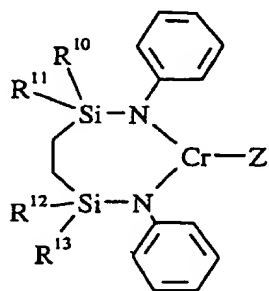
### Formula A1



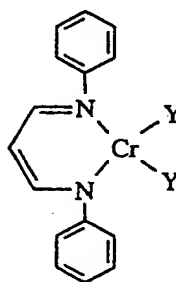
### Formula A2



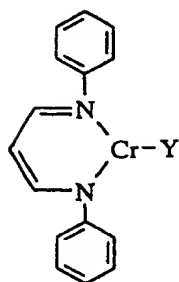
### Formula A3



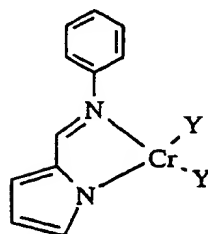
### Formula B 1



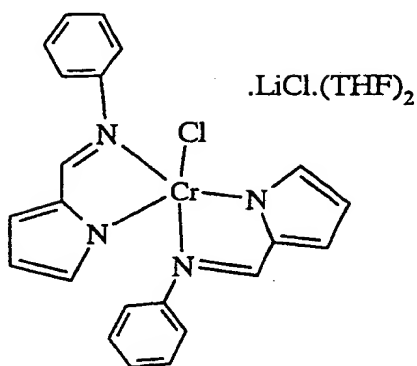
Formula B2



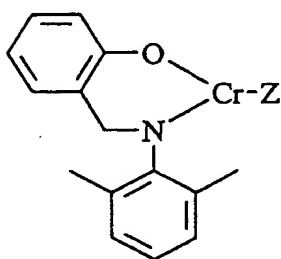
Formula B3



Formula B4



Formula C1



There are, of course many other structures which fall within the definition of the Formulae W, A, B, C, D, E and F of the catalysts of the present invention. In these Formulae, and for example in the Formulae A1, A2, A3, B1, B2, B3, B4 and C1 illustrated above, one or more of the hydrogen atoms pendant from the carbon atoms of the organic groups can be replaced by other atoms or groups, for example, methyl, ethyl, propyl, butyl, octyl, decyl, phenyl, naphthyl, acetyl, carboxyl, pyridino;

silyl, for example, trimethylsilyl, triethylsilyl: and suitable inorganic atoms or groups (eg halogen).

In Formula A3,  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$  and  $R^{13}$  are suitably selected from hydrogen, hydrocarbyl and heterohydrocarbyl. Preferably they are hydrogen or alkyl groups  
5 containing 1 to 6 carbon atoms.

The atom(s) or group(s) represented by Z in the units of Formula A and C are preferably selected from halide, sulphate, nitrate, thiolate, thiocarboxylate,  $BF_4^-$ ,  $PF_6^-$ , hydride, hydrocarbyloxy, carboxylate, hydrocarbyl, substituted hydrocarbyl, and heterohydrocarbyl. Examples of such atoms or groups are chloride, bromide, methyl  
10 , ethyl, propyl, butyl, octyl, decyl, phenyl, benzyl, methoxide, ethoxide, isopropoxide, tosylate, triflate, formate, acetate, phenoxide and benzoate.

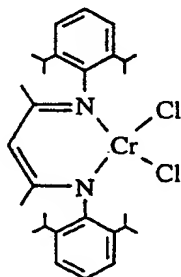
The atom(s) or group(s) represented by Y in the units of Formula W, B, D, E and F can be, if desired, selected from the same atoms or groups as the Z atoms or groups listed above. Additionally, in the case that  $m = 2$  (ie, when the Y group has a  
15 valency of 2) Y can be derived from, for example a dicarboxylic acid, a diol, a hydrocarbyl diradical, or an inorganic dibasic acid (eg sulphate).

The chromium compound complex units forming component (1) of the catalyst of the present invention may exist in the form of monomeric or dimeric forms. The solid crystalline complexes generally exist in the dimeric state. For  
20 example, Complex B5 illustrated below, is a complex chromium compound unit having a similar structure to that of Formula B2 above, but is substituted with isopropyl groups in the 2,6-positions on the phenyl substituents, and has two methyl groups on the group bridging the nitrogen atoms.

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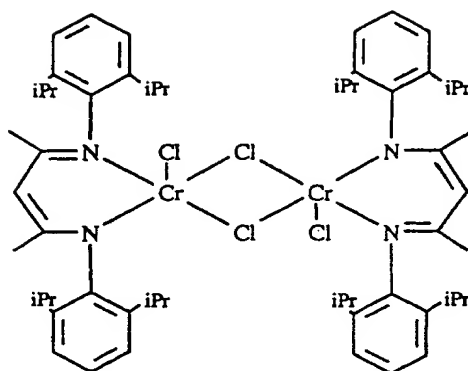
Complex B5

30



The solid form of Complex B5 is a crystalline dimer having the Formula B6  
35 (shown below):

Formula B6



The activator compound for the catalyst of the present invention is suitably selected from organoaluminium compounds and hydrocarbylboron compounds. Suitable organoaluminium compounds include trialkylaluminium compounds, for example, trimethylaluminium, triethylaluminium, tributylaluminium, tri-n-octylaluminium, ethylaluminium dichloride, diethylaluminium chloride and alumoxanes. Dialkyl aluminium halides are particularly preferred.

Alumoxanes are well known in the art as typically the oligomeric compounds which can be prepared by the controlled addition of water to an alkylaluminium compound, for example trimethylaluminium. Such compounds can be linear, cyclic or mixtures thereof. Commercially available alumoxanes are generally believed to be mixtures of linear and cyclic compounds. The cyclic alumoxanes can be represented by the formula  $[R^{33}AlO]_s$  and the linear alumoxanes by the formula  $R^{34}(R^{35}AlO)_s$ , wherein  $s$  is a number from about 2 to 50, and wherein  $R^{33}$ ,  $R^{34}$ , and  $R^{35}$  represent hydrocarbyl groups, preferably  $C_1$  to  $C_6$  alkyl groups, for example methyl, ethyl or butyl groups.

Examples of suitable hydrocarbylboron compounds are dimethylphenylammoniumtetra(phenyl)borate, trityltetra(phenyl)borate, triphenylboron, dimethylphenylammonium tetra(pentafluorophenyl)borate, sodium tetrakis[(bis-3,5-trifluoromethyl)phenyl]borate, tris(pentafluorophenyl) boron  $H^+(OEt)_2[(bis-3,5-trifluoromethyl)phenyl]borate$ , and trityltetra(pentafluorophenyl)borate.



In the preparation of the catalyst of the present invention the quantity of activating compound selected from organoaluminium compounds and hydrocarbylboron compounds to be employed is easily determined by simple testing, for example, by the preparation of small test samples which can be used to polymerise small quantities of the monomer(s) and thus to determine the activity of the produced catalyst. It is generally found that, for the organoaluminium activators the quantity employed is sufficient to provide 1 to 20,000 atoms, preferably 1 to 2000 atoms of aluminium per chromium atom in the compound of Formula W, A, B, C, D, E or F.

The catalyst of the present invention can, if desired, be supported on a support material, for example, silica, alumina, or zirconia, or on a polymer or prepolymer, for example polyethylene or polystyrene. Methods of preparation of supported catalysts are well known in the art. In the case that it is desired to use a supported catalyst the quantity of support material employed can vary widely, for example from 100,000 to 1 grams per gram of metal present in the defined chromium complex compound.

The present invention further provides a process for the polymerisation and copolymerisation of 1-olefins comprising contacting the monomeric olefin under polymerisation conditions with the catalyst of the present invention.

The polymerisation conditions can be, for example, solution phase, slurry phase or gas phase. If desired, the catalyst can be used to polymerise ethylene under high pressure/high temperature process conditions wherein the polymeric material forms as a melt in supercritical ethylene. Preferably the polymerisation is conducted under gas phase fluidised bed conditions. Suitable monomers for use in the polymerisation process of the present invention are, for example, ethylene, propylene, butene, hexene, methyl methacrylate, methyl acrylate, butyl acrylate, acrylonitrile, vinyl acetate, and styrene (the monomers in this list which are not 1-olefins can be used as comonomers if desired). The process can be, for example, homopolymerisation or copolymerisation of monomer selected from one or more of ethylene, propylene, 1-butene, 1-hexene, 4-methylpentene-1 and octene. Preferred monomers for homopolymerisation processes are ethylene and propylene. The catalyst is useful for copolymerising ethylene with other 1-olefins such as propylene, 1-butene, 1-hexene, 4-methylpentene-1, and octene.

Slurry phase polymerisation conditions or gas phase polymerisation conditions are particularly useful for the production of high, medium and low density grades of polyethylene. In these processes the polymerisation conditions can be batch, continuous or semi-continuous. In the slurry phase process and the gas phase process,

the catalyst is generally fed to the polymerisation zone in the form of a particulate solid. This solid can be, for example, an undiluted solid catalyst system formed from the chromium complex of the present invention and an activator, or can be the solid complex alone. In the latter situation, the activator can be fed to the polymerisation zone, for example as a solution, separately from or together with the solid complex. Preferably the catalyst system or the transition metal complex component of the catalyst system employed in the slurry polymerisation and gas phase polymerisation is supported on a support material. Most preferably the catalyst system is supported on a support material prior to its introduction into the polymerisation zone. Suitable support materials are, for example, silica, alumina, zirconia, talc, kieselguhr, or magnesia. Impregnation of the support material can be carried out by conventional techniques, for example, by forming a solution or suspension of the catalyst components in a suitable diluent or solvent, and slurrying the support material therewith. The support material thus impregnated with catalyst can then be separated from the diluent for example, by filtration or evaporation techniques.

In the slurry phase polymerisation process the solid particles of catalyst, or supported catalyst, are fed to a polymerisation zone either as dry powder or as a slurry in the polymerisation diluent. Preferably the particles are fed to a polymerisation zone as a suspension in the polymerisation diluent. The polymerisation zone can be, for example, an autoclave or similar reaction vessel, or a continuous loop reactor, e.g. of the type well-known in the manufacture of polyethylene by the Phillips Process. When the polymerisation process of the present invention is carried out under slurry conditions the polymerisation is preferably carried out at a temperature above 0°C, most preferably above 15°C. The polymerisation temperature is preferably maintained below the temperature at which the polymer commences to soften or sinter in the presence of the polymerisation diluent. If the temperature is allowed to go above the latter temperature, fouling of the reactor can occur. Adjustment of the polymerisation within these defined temperature ranges can provide a useful means of controlling the average molecular weight of the produced polymer. A further useful means of controlling the molecular weight is to conduct the polymerisation in the presence of hydrogen gas which acts as chain transfer agent. Generally, the higher the concentration of hydrogen employed, the lower the average molecular weight of the produced polymer.

The use of hydrogen gas as a means of controlling the average molecular weight of the polymer or copolymer applies generally to the polymerisation process of

the present invention. For example, hydrogen can be used to reduce the average molecular weight of polymers or copolymers prepared using gas phase, slurry phase or solution phase polymerisation conditions. The quantity of hydrogen gas to be employed to give the desired average molecular weight can be determined by simple  
5 "trial and error" polymerisation tests.

Methods for operating gas phase polymerisation processes are well known in the art. Such methods generally involve agitating (eg by stirring, vibrating or fluidising) a bed of catalyst, or a bed of the target polymer (ie polymer having the same or similar physical properties to that which it is desired to make in the  
10 polymerisation process) containing a catalyst, and feeding thereto a stream of monomer at least partially in the gaseous phase, under conditions such that at least part of the monomer polymerises in contact with the catalyst in the bed. The bed is generally cooled by the addition of cool gas (eg recycled gaseous monomer) and/or volatile liquid (eg a volatile inert hydrocarbon, or gaseous monomer which has been  
15 condensed to form a liquid). The polymer produced in, and isolated from, gas phase processes forms directly a solid in the polymerisation zone and is free from, or substantially free from liquid. As is well known to those skilled in the art, if any liquid is allowed to enter the polymerisation zone of a gas phase polymerisation process the quantity of liquid is small in relation to the quantity of polymer present in the  
20 polymerisation zone. This is in contrast to "solution phase" processes wherein the polymer is formed dissolved in a solvent, and "slurry phase" processes wherein the polymer forms as a suspension in a liquid diluent.

The gas phase process can be operated under batch, semi-batch, or so-called "continuous" conditions. It is preferred to operate under conditions such that  
25 monomer is continuously recycled to an agitated polymerisation zone containing polymerisation catalyst, make-up monomer being provided to replace polymerised monomer, and continuously or intermittently withdrawing produced polymer from the polymerisation zone at a rate comparable to the rate of formation of the polymer, fresh catalyst being added to the polymerisation zone to replace the catalyst withdrawn from  
30 the polymerisation zone with the produced polymer. Gas phase fluidised bed polymerisation conditions are preferred in the polymerisation process of the present invention..

Methods for operating gas phase fluidised bed processes for making polyethylene and ethylene copolymers are well known in the art. The process can be  
35 operated, for example, in a vertical cylindrical reactor-equipped with a perforated

distribution plate to support the bed and to distribute the incoming fluidising gas stream through the bed. The fluidising gas circulating through the bed serves to remove the heat of polymerisation from the bed and to supply monomer for polymerisation in the bed. Thus the fluidising gas generally comprises the monomer(s) normally together with some inert gas (eg nitrogen) and optionally with hydrogen as molecular weight modifier. The hot fluidising gas emerging from the top of the bed is led optionally through a velocity reduction zone (this can be a cylindrical portion of the reactor having a wider diameter) and, if desired, a cyclone and or filters to disentrain fine solid particles from the gas stream. The hot gas is then led to a heat exchanger to remove at least part of the heat of polymerisation. Catalyst is preferably fed continuously or at regular intervals to the bed. At start up of the process, the bed comprises fluidisable polymer which is preferably similar to the target polymer. Polymer is produced continuously within the bed by the polymerisation of the monomer(s). Preferably means are provided to discharge polymer from the bed continuously or at regular intervals to maintain the fluidised bed at the desired height. The process is generally operated at relatively low pressure, for example, at 10 to 50 bars, and at temperatures for example, between 50 and 120 °C. The temperature of the bed is maintained below the sintering temperature of the fluidised polymer to avoid problems of agglomeration.

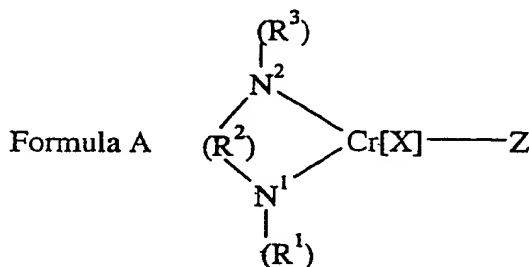
In the gas phase fluidised bed process for polymerisation of olefins the heat evolved by the exothermic polymerisation reaction is normally removed from the polymerisation zone (ie, the fluidised bed) by means of the fluidising gas stream as described above. The hot reactor gas emerging from the top of the bed is led through one or more heat exchangers wherein the gas is cooled. The cooled reactor gas, together with any make-up gas, is then recycled to the base of the bed. In the gas phase fluidised bed polymerisation process of the present invention it is desirable to provide additional cooling of the bed (and thereby improve the space time yield of the process) by feeding a volatile liquid to the bed under conditions such that the liquid evaporates in the bed thereby absorbing additional heat of polymerisation from the bed by the "latent heat of evaporation" effect. When the hot recycle gas from the bed enters the heat exchanger, the volatile liquid can condense out. In one embodiment of the present invention the volatile liquid is separated from the recycle gas and reintroduced separately into the bed. Thus, for example, the volatile liquid can be separated and sprayed into the bed. In another embodiment of the present invention the volatile liquid is recycled to the bed with the recycle gas. Thus the volatile liquid

can be condensed from the fluidising gas stream emerging from the reactor and can be recycled to the bed with recycle gas, or can be separated from the recycle gas and sprayed back into the bed.

The method of condensing liquid in the recycle gas stream and returning the mixture of gas and entrained liquid to the bed is described in EP-A-0089691 and EP-A-0241947. It is preferred to reintroduce the condensed liquid into the bed separate from the recycle gas using the process described in our US Patent 5541270, the teaching of which is hereby incorporated into this specification.

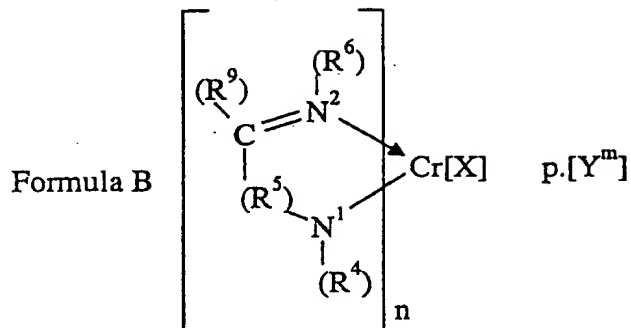
When using the catalysts of the present invention under gas phase polymerisation conditions, the catalyst, or one or more of the components employed to form the catalyst can, for example, be introduced into the polymerisation reaction zone in liquid form, for example, as a solution in an inert liquid diluent. Thus, for example, the transition metal component, or the activator component, or both of these components can be dissolved or slurried in a liquid diluent and fed to the polymerisation zone. Under these circumstances it is preferred the liquid containing the component(s) is sprayed as fine droplets into the polymerisation zone. The droplet diameter is preferably within the range 1 to 1000 microns. EP-A-0593083, the teaching of which is hereby incorporated into this specification, discloses a process for introducing a polymerisation catalyst into a gas phase polymerisation. The methods disclosed in EP-A-0593083 can be suitably employed in the polymerisation process of the present invention if desired.

The present invention further provides a novel complex chromium compound having the Formula A, or a dimer thereof:



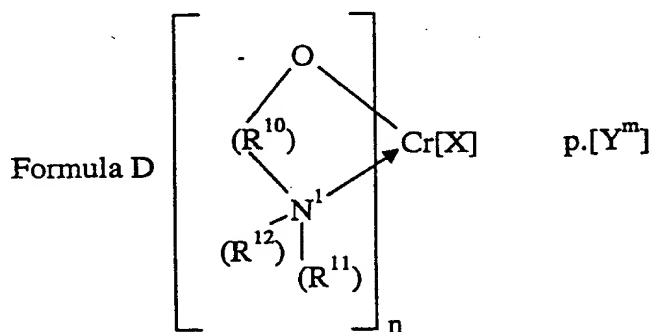
wherein  $R^2$ , is an organic group comprising at least a saturated or unsaturated chain;  $R^1$  and  $R^3$  are organic groups; two or more of the defined R groups are optionally linked to one another;  $N^1$  and  $N^2$  are nitrogen atoms; X is the oxidation state of the chromium; Z is a univalent atom or group.

The present invention further provides a novel complex chromium compound having the Formula B, or a dimer thereof:



wherein  $\text{R}^5$  is an organic group comprising at least a saturated or unsaturated chain;  $\text{R}^4$  and  $\text{R}^6$  are organic groups;  $\text{R}^9$  is hydrogen or an organic groups; two or more of the defined R groups are optionally linked to one another;  $\text{N}^1$  and  $\text{N}^2$  are nitrogen atoms; X is the oxidation state of the chromium and is 3; Y is an atom or group having a valency of m, where  $m = 1$  or  $2$ ; p represents the number of atoms or groups of Y present in the complex unit; n is 1 or 2; and p is zero or an integer which satisfies the relationship  $p = (X-n)/m$ .

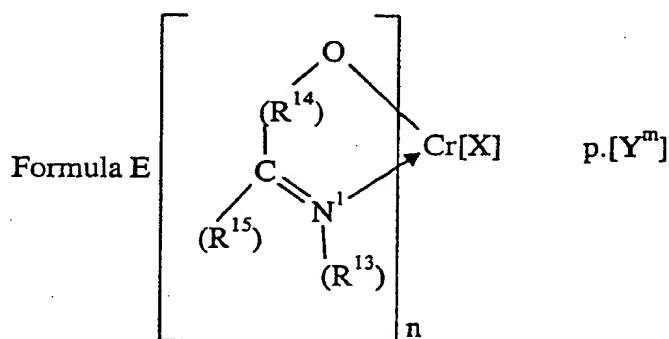
The present invention further provides a novel complex chromium compound having the Formula D, or a dimer thereof:



wherein  $\text{R}^{10}$  is an organic group comprising at least a saturated or unsaturated chain;  $\text{R}^{11}$  is an organic group;  $\text{R}^{12}$  is independently hydrogen or an organic group; two or more of the defined R groups are optionally linked to one another;  $\text{N}^1$  is a nitrogen atom; O is an oxygen atom; X is the oxidation state of the chromium and is 2; Y is an atom or group having a valency of m, where  $m = 1$  or  $2$ ; p represents the number of

atoms or groups of Y present in the complex unit; n is 1 or 2; and p is zero or an integer which satisfies the relationship  $p = (X-n)/m$ .

The present invention further provides a novel complex chromium compound having the Formula E, or a dimer thereof:



wherein  $R^{14}$  is an organic group comprising at least a saturated or unsaturated chain;  $R^{13}$  is an organic group;  $R^{15}$  is hydrogen or an organic group; two or more of the defined R groups are optionally linked to one another;  $N^1$  is a nitrogen atom; O is an oxygen atom; X is the oxidation state of the chromium and is 2; Y is an atom or group having a valency of m, where  $m = 1$  or  $2$ ; p represents the number of atoms or groups of Y present in the complex unit; n is 1 or 2; and p is zero or an integer which satisfies the relationship  $p = (X-n)/m$ .

In the novel complex chromium compounds of the present invention listed above, in addition to the defined ligand or ligands, the chromium compound can optionally comprise one or more neutral molecules coordinated to the chromium, for example, solvent molecules. Examples of such neutral molecules are ethers, amines, nitriles and esters, for example, tetrahydrofuran, acetonitrile, formdimethylamide and methyl benzoate.

In the novel complex chromium compounds of the present invention the atom(s) or group(s) represented by Z in the units of Formula A are preferably selected from halide, sulphate, nitrate, thiolate, thiocarboxylate,  $BF_4^-$ ,  $PF_6^-$ , hydride, hydrocarbyloxy, carboxylate, hydrocarbyl, substituted hydrocarbyl, and heterohydrocarbyl. Examples of such atoms or groups are chloride, bromide, methyl, ethyl, propyl, butyl, octyl, decyl, phenyl, benzyl, methoxide, ethoxide, isopropoxide, tosylate, triflate, formate, acetate, phenoxide and benzoate; and the atom(s) or group(s) represented by Y in the units of Formula B, D and E can be, if desired, selected from the same atoms or groups as the Z atoms or groups listed above.

Additionally, in the case that  $m = 2$  (ie, when the Y group has a valency of 2) Y can be derived from, for example a dicarboxylic acid, a diol, a hydrocarbyl diradical, or an inorganic dibasic acid (eg sulphate). The preferences as regards the R groups present in the novel complex chromium compounds of the present invention are the same as those expressed above in relation to the catalysts of the present invention.

The present invention is illustrated in the following Examples which describe the preparation of chromium complex compounds, their activation with organometallic activators to form polymerisation catalysts and the use of these catalysts to polymerise ethylene in accordance with the present invention. A summary of the polymerisation tests is provided Tables 1 and 2.

### Example 1

#### 1.1 Synthesis of "Intermediate IA4" (see Formula below)

To a suspension of lithium 2,6-dimethylanilide (9.28 g, 69.71 mmol) in Et<sub>2</sub>O (150 ml) was added a solution of  $\alpha,\alpha'$ -dichloro-o-xylene (5.81 g, 33.20 mmol) in Et<sub>2</sub>O (75 ml) at -78°C. After 30 minutes the solution was warmed to room temperature and stirred overnight. The solution gradually turned orange with a pale white precipitate. Filtration through celite removed LiCl and the resulting orange viscous oil was dried for several hours before extracting with pentane. The solution was filtered again to remove any residual traces of LiCl. The resulting solution concentrated by 2/3 and placed in the freezer at -20°C. After 2 days crystalline material was obtained after filtration from the mother liquor and drying in vacuo (5.55 g 16.12 mmol, 49%). The structure of the product was confirmed by spectroscopic analysis and microanalysis.

The dilithium salt of "Intermediate IA4" was generated by reaction of the parent amine with two equivalents of n-butyllithium in THF at -78°C.

#### 1.2 Synthesis of chromium complex (see Formula A4 below)

CrCl<sub>3</sub>.(THF)<sub>3</sub> (1.45 g 3.9 mmol) and dilithiated "Intermediate IA4" (1.38 g, 3.9 mmol) were charged into a Schlenk flask. The flask was cooled to -78 °C before the addition of THF (40 ml). The solution immediately turned dark brown green. After 20 minutes the solution was warmed to room temperature and stirred overnight. The solvent was removed in vacuo and allowed to dry for several hours to remove all traces of THF. Toluene (30 ml) was added to the dark green residue and stirred for 3 hours. The solution was filtered to remove lithium chloride and reduced to 5 ml. Pentane (50 ml) was added resulting in the precipitation of a light green microcrystalline powder. The supernatant liquid was removed and the solids washed



with pentane (10 ml) before drying in vacuo overnight to give the complex of Formula A4 (1.11 g, 66 %).

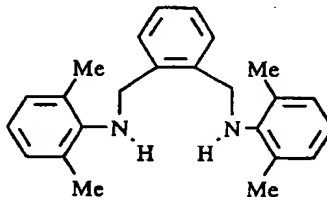
It will be noted that the Formula A4 compound is a dimer comprising two units in accordance with the Formula A complex of the present invention.

5 1.3 Polymerisation of ethylene using a catalyst prepared from the Formula A4 complex and DEAC

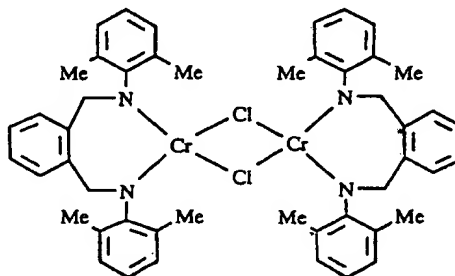
A 1.8 M solution of diethylaluminium chloride (DEAC) in toluene (0.33 ml, 0.6 mmol) was added via syringe to a stirred suspension of the Formula A4 complex (26 mg, 0.06 mmol) in toluene (40 ml). DEAC is commercially available from Aldrich.

10 The produced catalyst solution was degassed under reduced pressure and back-filled with an atmosphere of ethylene. During the run time of 60 minutes the solution was left open to a supply of ethylene at one atmosphere and stirred vigorously at 25°C. The polymerisation was terminated by the addition of dilute HCl (ca. 40 ml) and then stirred for 30 minutes to dissolve the alkylaluminium residues. Solid polyethylene  
15 was filtered from the reaction, washed with an acidified methanol solution and dried in vacuo at 40°C overnight. Yield 2.63 g. Activity was 44 gmmol<sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup> (per Cr centre).

20 Intermediate IA4



25 Formula A4



## Example 2

### 2.1 Synthesis of "Intermediate IA5(a)" (see formula below)

Pyrrole-2-carboxaldehyde (5.10 g, 53.63 mmol) was dissolved in ethanol (60 ml). Freshly distilled 2,6-dimethylaniline (7.3 ml, 7.15 g, 59.00 mmol) was added to the solution together with MgSO<sub>4</sub>. The solution was heated at reflux overnight. The MgSO<sub>4</sub> was filtered from the solution and the volatiles removed under reduced pressure. The produced "Intermediate IA5(a)" (a pyrrole-imine) was isolated as a pale beige solid (8.20 g, 41.34 mmol, 77%). This material recrystallised by dissolving in Et<sub>2</sub>O and placing the solution in the freezer at -20°C overnight. The structure of the product was confirmed by NMR and microanalysis.

### 2.2 Synthesis of "Intermediate IA5(b)" (see formula below)

To a suspension of LiAlH<sub>4</sub> (3.50 g, 90.80 mmol) in Et<sub>2</sub>O (150 ml) was added "Intermediate IA5(a)" (3.00 g, 15.13 mmol) in Et<sub>2</sub>O (50 ml) at 0°C. Vigorous evolution of gas was observed. The suspension was stirred at room temperature for 30 minutes. The reaction was quenched at 0°C by the dropwise addition of water (20 ml). The inorganic salts were filtered off and the organic fraction dried over MgSO<sub>4</sub>. Removal of the volatiles under reduced pressure afforded an off-white solid (2.70 g, 13.48 mmol, 89 %). The product "Intermediate IA5(b)" was found to be pure by <sup>1</sup>H NMR analysis.

### 2.3 Synthesis of chromium complex (see Formula A5 below)

To a THF (40 ml) solution of "Intermediate IA5(b)" (1.52 g, 7.59 mmol) was added n-butyllithium (10 ml, 15.94 mmol) at -78°C. The solution was warmed to room temperature for 1 hour. The solution turned orange. The solution of dilithiated "Intermediate IA5(b)" was added to a suspension of CrCl<sub>3</sub>·(THF)<sub>3</sub> (2.84 g, 7.59 mmol) in THF (30 ml) at -78°C. The solution immediately turned orange-red. After 20 min the solution was warmed to room temperature and stirred overnight. Solvent was removed under reduced pressure and allowed to dry overnight to remove all traces of THF. Toluene (30 ml) was added to the dark red residue and stirred for 3 hours. The solution was filtered to remove lithium chloride, and the volatiles were removed in vacuo to give the complex of Formula A5 (1.89 g, 87%).

### 2.4 Polymerisation of ethylene using a catalyst prepared from the Formula A5 complex and DEAC

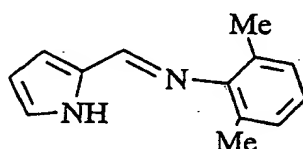
Preparation of the catalyst and polymerisation of ethylene were carried out substantially as described in Example 1 except that the catalyst was prepared from the Formula A5 complex (9 mg, 0.03 mmol). The run time was 30 minutes. Solid

polyethylene was produced. The yield was 0.53 g. corresponding to an activity of 35  $\text{gmmol}^{-1} \text{h}^{-1} \text{bar}^{-1}$  (per Cr centre).

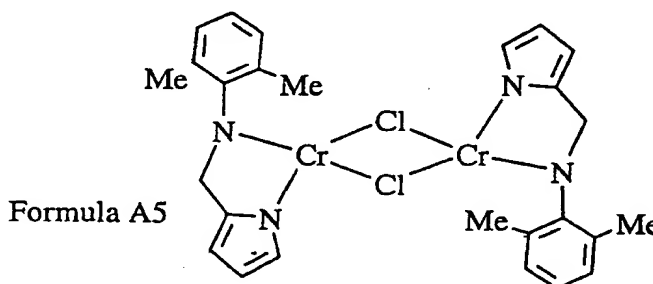
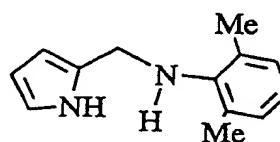
## 2.5 Polymerisation of ethylene using a catalyst prepared from the Formula A5 complex and DMAC

- 5 Preparation of the catalyst and polymerisation of ethylene were carried out substantially as described in Example 1 except that the catalyst was prepared from metal the Formula A5 complex (9 mg, 0.03 mmol) and 1.0 M solution of DMAC (0.6 ml, 0.6 mmol) in toluene. The run time was 30 minutes. Solid polyethylene was produced. The yield was 0.81 g corresponding to an activity of 54  $\text{gmmol}^{-1} \text{h}^{-1} \text{bar}^{-1}$  (per Cr centre).

Intermediate IA5(a)



Intermediate IA5(b)



### Example 3

#### 3.1 Synthesis of "Intermediate IA6" (see formula below)

- To a diethyl ether solution of lithium 2,6-dimethylaniline (8.27 g, 62.16 mmol) (80 ml) was added 1,2-bis(chlorodimethylsilyl)ethane (6.37 g, 29.60 mmol) in diethyl ether (50 ml) at  $-78^{\circ}\text{C}$ . The solution turned dark orange upon warming, and was stirred for 12 hours at room temperature. The volatiles were removed and the resulting solid washed with petroleum ether (2 x 15) ml at  $-78^{\circ}\text{C}$ . The produced "Intermediate IA6" was isolated as a yellow-orange solid and was dried in vacuo overnight (10.07 g, 26.17 mmol, 88%).

The product was confirmed by NMR to correspond to the required structure for "Intermediate IA6".

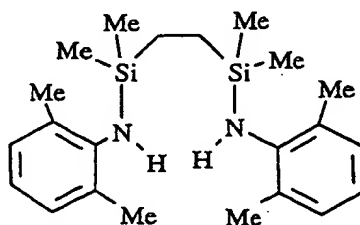
The dilithium salt of "Intermediate IA6" was generated by reaction with two equivalents of n-butyllithium in THF at -78°C.

5 3.2 Synthesis of chromium complex (see Formula A6 below)

CrCl<sub>3</sub>•(THF)<sub>3</sub> (0.73 mg, 1.94 mmol) and the dilithiated "Intermediate IA6" (0.81 mg, 2.04 mmol) were charged into a Schlenk flask in the glove box. The solids were cooled to -78°C before the addition of THF (30 ml). The solution immediately turned deep olive green. After 20 minutes the solution was warmed to room  
10 temperature and stirred overnight after which the solution had turned dark brown. The volatiles were removed in vacuo and resulting green-brown solids extracted with pentane (30 ml) to remove the lithium chloride. Filtration was repeated at -78°C to remove a persistent brown impurity. Removal of the volatiles under reduced pressure afforded the product of Formula A6 which was mustard yellow-green waxy solid.  
15 The solid dried for 2 hours The yield was 0.50 g, 55%).

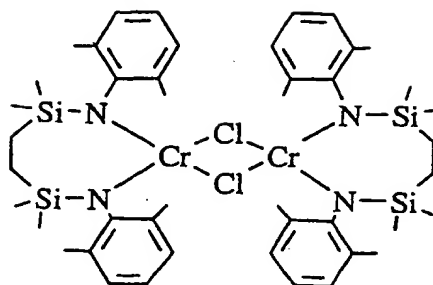
3.3 Polymerisation of ethylene using a catalyst prepared from the Formula A6 complex and DEAC

Preparation of the catalyst and polymerisation of ethylene were carried out substantially as described in Example 1 except that the catalyst was prepared from the  
20 Formula A6 complex (28 mg, 0.06 mmol). The run time was 60 minutes. Solid polyethylene was produced. The yield was 0.83 g. corresponding to an activity of 14 gmmol<sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup> (per Cr centre).



Intermediate IA6

Formula A6

**Example 4****4.1** Synthesis of "Intermediate IB7(a)" (see formula below)

In a three-step procedure 2,4-pentanedione was treated with one equivalent of 2,6-diisopropylaniline and refluxed in the presence of several drops of formic acid for 2 hours. After cooling to room temperature diethylether (20 ml) was introduced and the solution cooled to  $-78^{\circ}\text{C}$  to give white crystals of 2-pentanone-4-(2,6-diisopropylphenyl)imine ("Intermediate IB7(a)"). The yield was 80%.

**4.2** Synthesis of "Intermediate IB7(b)" (see formula below)

Equimolar quantities of a solution in absolute ethanol of "Intermediate IB7(a)" and the HCl adduct of 2,6-diisopropylaniline were refluxed for 12 h. The product was the HCl adduct of "Intermediate IB7(b)". The latter was isolated in high yield by treatment with ammonia gas of a solution of the adduct in dichloromethane. The structure and purity of "Intermediate IB7(b)" were confirmed by microanalysis, FAB mass spectrum and NMR.

**4.3** Synthesis of chromium complex (see Formula B7 below)

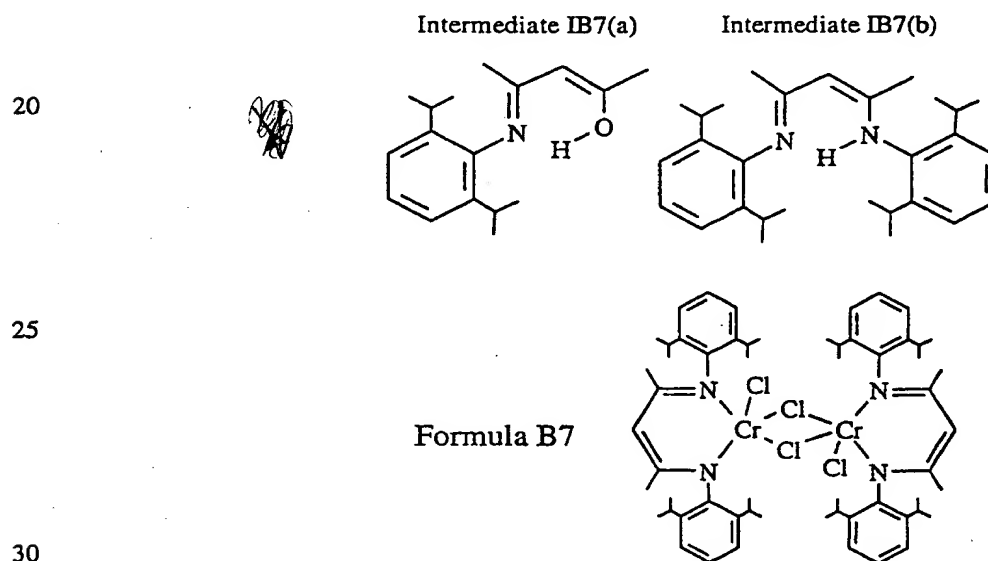
Tetrahydrofuran (THF) (40 ml) was added to a mixture of the lithium salt of "Intermediate IB7(b)" (1.13 g, 2.7 mmol) and  $\text{CrCl}_3 \cdot (\text{THF})_3$  (1.00 g, 2.7 mmol) in a Schlenk vessel. The mixture was stirred overnight at room temperature during which time the solution became olive green. The THF was removed under reduced pressure, then pentane (40 ml) was added and the solution stirred. Filtration of the lithium salts and drying of the filtrate overnight gave the complex of Formula A8 (1.16 g, 80%). Microanalysis, FAB Mass spectrum and single crystal X-ray diffraction confirm the

structure of the complex. The single crystal X-ray diffraction study revealed the structure to be dimeric in the solid state (see Figure 1).

$\text{CrCl}_3 \cdot (\text{THF})_3$  was made by a published procedure (see J. Shamir, *Inorg. Chim. Acta*, 1989, 156, 163).

5 4.4 Polymerisation of ethylene using a catalyst prepared from the Formula B7 complex and DEAC

A 1.8 M solution of diethylaluminium chloride (DEAC) in toluene (0.50 ml, 0.9 mmol, 30 equivalents) was added via syringe to a stirred suspension of the Formula B7 complex (16 mg, 0.015 mmol) in toluene (40 ml). The produced catalyst solution was degassed under reduced pressure and back-filled with an atmosphere of ethylene. During the run time of 60 minutes the solution was left open to a supply of ethylene at one atmosphere and stirred vigorously at 25°C. The polymerisation was terminated by the addition of dilute HCl (ca. 40 ml) and then stirred for 30 minutes to dissolve the alkylaluminium residues. Solid polyethylene was filtered from the reaction, washed with an acidified methanol solution and dried in vacuo at 40°C overnight. Yield 2.25 g. Activity was  $75 \text{ gmmol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$  [per Cr centre].



Example 5

5.1 Synthesis of chromium complex (see Formula B8 below)

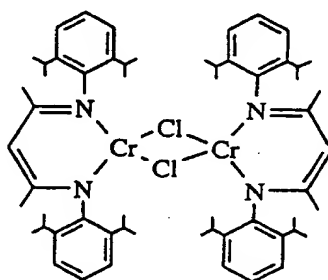
The complex of Formula B7 (1.44 g, 1.33 mmol) was dissolved in THF (40 ml) giving an olive green solution. On cooling to -78°C benzylmagnesium chloride (2 M solution in THF) (1.34 ml, 2.66 mmol) was added dropwise. The solution was stirred

overnight and then 1,4-dioxane (2 ml) was introduced. Further stirring for 2 hours was followed by filtration and concentration to half volume of the filtrate. Cooling of the filtrate to  $-18^{\circ}\text{C}$  gave lime green crystals of the complex of Formula B8 (0.66 g, 49 %). The structure was confirmed by microanalysis, FAB mass spectrum and single crystal X-ray diffraction. The structure was dimeric in the solid state (see attached Figure 2).

## 5.2 Polymerisation of ethylene using a catalyst prepared from the Formula B8 complex and DEAC

Preparation of the catalyst and polymerisation of ethylene were carried out substantially as described above except that the catalyst was prepared from the Formula B8 complex (15.1 mg, 0.015 mmol). The run time was 60 minutes. Solid polyethylene was produced. Yield 2.16 g. Activity was  $72 \text{ gmmol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$  [per Cr centre].

Formula B8



## Example 6

### 6.1 Synthesis of "Intermediate IB9" (see Formula below)

Pyrrole-carboxyaldehyde (1.0 g, 10.5 mmol) was dissolved in diethyl ether (30 ml) and 2,6-diisopropylaniline (2.0 ml, 10.6 mmol) and a few drops of formic acid introduced. After refluxing for 2 hours the solution was cooled and anhydrous magnesium sulphate added. Filtration and cooling of the filtrate to  $-78^{\circ}\text{C}$  gave "Intermediate IB9" in 90% yield. The structure was confirmed by microanalysis, EI mass spectrum and NMR.

Pyrrole-carboxyaldehyde and 2,6-diisopropylaniline were supplied by Aldrich Chemicals.

### 6.2 Synthesis of chromium complex (see Formula B9 below)

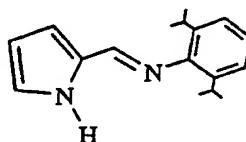
THF (40 ml) was added to a mixture of the lithium salt of "Intermediate IB9" (1.40 g, 5.4 mmol) and  $\text{CrCl}_3 \cdot (\text{THF})_3$  (1.00 g, 2.7 mmol) at  $-78^{\circ}\text{C}$  in a Schlenk vessel. The

mixture was allowed to warm to room temperature and stirred overnight during which time the solution became red. The THF was removed under reduced pressure and pentane (40 ml) added and the solution stirred. Filtration of the lithium salts and drying of the filtrate overnight gave the complex of Formula B10 (0.75 g, 75%). The structure was confirmed by FAB mass spectrum and single crystal X-ray diffraction. The latter revealed that the product was a lithium chloride adduct (see Figure 3).

### 6.3 Polymerisation of ethylene using a catalyst prepared from the Formula B9 complex and DEAC

Preparation of the catalyst and polymerisation of ethylene were carried out substantially as described above except that the catalyst was prepared from the Formula B9 complex (12 mg, 0.015 mmol) and DEAC (0.50 ml, 0.9 mmol, 30 equivalents). The run time was 0.5 hour. Solid polyethylene was collected. Yield 1.04 g. Activity was  $69 \text{ gmmol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$  [per Cr centre].

Intermediate IB9



Formula B9

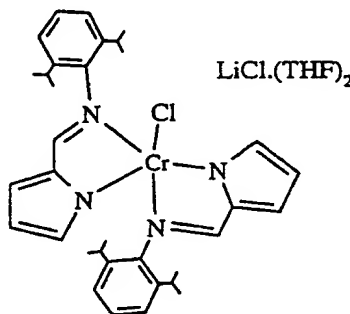




TABLE 1				
Example No.	Metal Complex Formula	Co-catalyst	Amount of polyethylene g	Activity (note 1)
1.3	A4	DEAC	2.63	44
2.4	A5	DEAC	0.53	35
2.5	A5	DMAC	0.81	54
3.3	A6	DEAC	0.83	14
4.4	B7	DEAC	2.25	75
5.2	B8	DEAC	2.16	72
6.3	B9	DEAC	1.04	69

#### Notes on Table 1

Activity is expressed as  $\text{g mmol}^{-1} \text{h}^{-1} \text{bar}^{-1}$ .

#### Examples 7 to 12

These Examples illustrate the preparation of chromium compounds in accordance with the present invention and their use as catalysts to polymerise ethylene. The polymerisation tests are described following Example 12 and the results are shown in Table 2.

#### Example 7

##### 7.1 Synthesis of "Intermediate ID2(a)" (see Formula below)

3,5-di-tert-butyl-2-hydroxybenzaldehyde (7.04 g, 30.04 mmol) was dissolved in methanol (120 ml). Freshly distilled 2,6-dimethylaniline (7.3 ml, 7.15 g, 59.0 mmol) was added to the solution together with  $\text{MgSO}_4$  drying agent. The solution was heated at reflux for 5 hours. The  $\text{MgSO}_4$  was filtered from the yellow solution which was reduced to 25 ml by evaporation under reduced pressure. The product which was a yellow crystalline material (7.54 g, 22.37 mmol, 74%) was isolated from the solution upon standing at room temperature for two days. The structure of the produced

"Intermediate ID2(a)" was confirmed by spectroscopic analysis and microanalysis

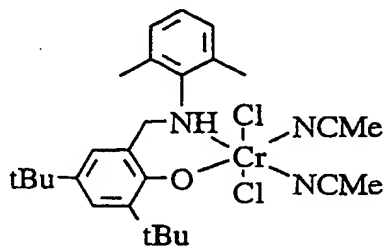
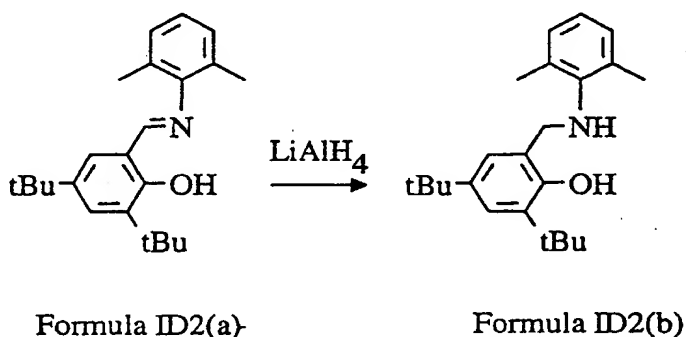
##### 7.2 Synthesis of "Intermediate ID2(b)" (see Formula below)

To a suspension of  $\text{LiAlH}_4$  (1.34 g, 35.6 mmol) in  $\text{Et}_2\text{O}$  (100 ml) was added "Intermediate ID2(a)" (4.00 g, 11.85 mmol) in  $\text{Et}_2\text{O}$  (50 ml) at  $0^\circ\text{C}$ . Vigorous evolution of gas was observed. The suspension was stirred at room temperature for 30 minutes. The reaction was quenched at  $0^\circ\text{C}$  by the dropwise addition of water (10

ml). The inorganic salts were removed by filtration and the organic fraction dried over  $\text{MgSO}_4$ . Removal of the volatiles under reduced pressure afforded "Intermediate ID2(b)" as an off-white solid product. The structure and purity of the product was confirmed by NMR.

5 7.3 Synthesis of chromium complex {Cr[3,5-(CMe<sub>3</sub>)<sub>2</sub>-2-(O)C<sub>6</sub>H<sub>2</sub>.CH<sub>2</sub>NHAr]}[( $\eta^1$ -NCCH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>](see Formula D2 below)  
(Ar = C<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub>)

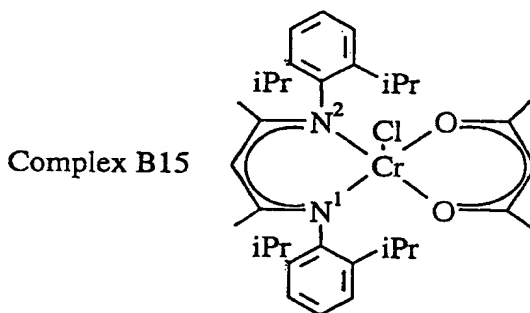
The ligand (2.00 g, 5.89 mmol) of Formula ID2(b) and NaH (0.31 g, 12.96 mmol) in THF (45 ml) were refluxed for 12 hours. On cooling, the suspension was filtered into  
 10  $\text{CrCl}_3(\text{THF})_3$  (2.21 g, 5.98 mmol) in THF (25 ml) at  $-78^\circ\text{C}$ . The solution was stirred at room temperature for 12 hours. After removal of volatiles *in vacuo*, the solid residue was extracted into toluene (75 ml). Recrystallisation from acetonitrile/heptane (1:3) afforded green prisms of the chromium complex of Formula D2 on prolonged standing (3-4 days) at ambient temperature. Yield 1.65 g, 51 %.



The complex of Formula D2 is solvated in the solid state by the presence of two molecules of NCMe (acetonitrile) present as substituents co-ordinated on the Cr  
 35 atom.

Example 88.1 Synthesis of chromium complex  $\{Cr(CH\{C(Me)NAr\}_2)(acac)Cl\}$  (see Formula B15 below) (Ar = 2,6-*i*-Pr<sub>2</sub>-Ph)

To a THF (40 ml) solution of the lithium salt of  $CH_2\{C(Me)NAr\}_2$  (Ar = 2,6-*i*-Pr<sub>2</sub>-Ph) (1.13 g, 2.67 mmol) at -78°C was added  $CrCl_3 \cdot 3THF$  (1.0 g, 2.67 mmol). The solution was allowed to warm to room temperature and stirred for 3 hours. The produced dark green THF solution was cooled to -78°C and the lithium salt of 2,4-pentanedione (acac-H) (0.283 g, 2.67 mmol) was added. The solutions were allowed to warm to room temperature and stirred for a further 12 hours. After removal of the solvent under reduced pressure pentane (60 ml) was introduced and the lithium salts filtered. Concentration of the filtrate to half volume and cooling to -10°C overnight gave the complex of Formula B15 (45%) as red crystals. Microanalytical data and FAB mass spectra confirmed the structure of complex B15.

Example 99.1 Synthesis of chromium complex  $\{Cr(CH\{C(Me)NAr\}_2)(RCOO)(THF)Cl\}$  (see Formula B16 below wherein R is methyl (Formula B16a) or phenyl (Formula B16b))9.1a Preparation of Formula B16a Complex

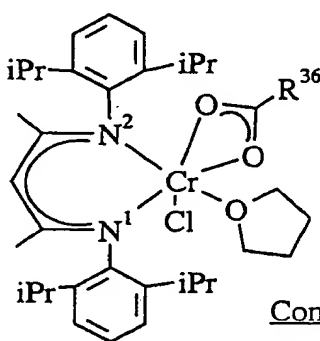
To a THF (40 ml) solution of the lithium salt of  $CH_2\{C(Me)NAr\}_2$  (1.13 g, 2.67 mmol) at -78°C was added  $CrCl_3 \cdot 3THF$  (1.0 g, 2.67 mmol). The Ar group was 2,6-*i*-Pr<sub>2</sub>-Ph. The solution was allowed to warm to room temperature and stirred for 3 hours. The produced dark green THF solution was cooled to -78°C and sodium acetate (0.219 g, 2.67 mmol) was added. The solution was allowed to warm to room temperature and stirred for a further 12 hours. After removal of the solvent under reduced pressure pentane (60 ml) was introduced and the lithium salt filtered. Concentration of the filtrate to half

volume and cooling to  $-10^{\circ}\text{C}$  overnight gave Formula B16a complex (45%) as green crystals.

#### 9.1b Preparation of Formula B16b Complex

The procedure of 9.1a was repeated except that sodium benzoate (0.384 g, 2.67 mmol) was used instead of sodium acetate. Green crystals of the complex of Formula B16b were isolated. The yield was 49%.

Microanalytical data and FAB mass spectra on the complexes B16a and B16b confirmed the structure.



Complex B16

Complex B16a;  $\text{R}^{36}$  = methyl

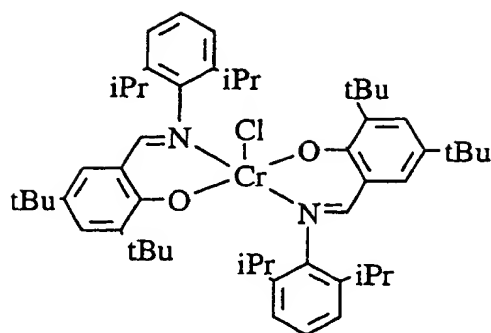
Complex B16b;  $\text{R}^{36}$  = phenyl

#### 20 Example 10

##### 10.1 Preparation of $\{\text{Cr}[3,5-(\text{CMe}_3)_2-2-(\text{O})\text{C}_6\text{H}_2\text{CH}=\text{NAr}]\}_2\text{Cl}\}$

See Formula E3 below (Ar = 2,6-*i*-Pr<sub>2</sub>-Ph)

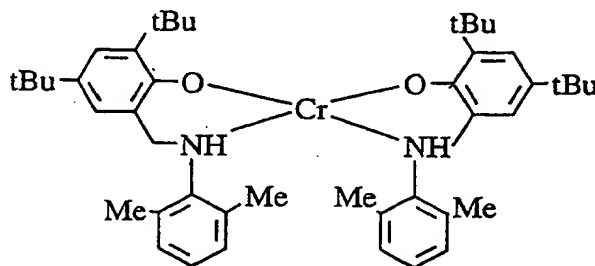
The ligand 3,5-( $\text{CMe}_3$ )<sub>2</sub>-2-(OH) $\text{C}_6\text{H}_2\text{CH}=\text{NAr}$  (2.10 g, 5.34 mmol) was dissolved in THF (40 ml) and cooled to  $-78^{\circ}\text{C}$ . *n*-BuLi (3.34 ml, 5.34 mmol) was added dropwise to this solution and allowed to warm to room temperature and stirred for 0.5 hours and then re-cooled to  $-78^{\circ}\text{C}$ .  $\text{CrCl}_3 \cdot 3\text{THF}$  (1.0 g, 2.67 mmol) was added to this cooled solution and the reaction mixture stirred overnight at room temperature. After removal of the solvent under reduced pressure pentane (60 ml) was introduced and the lithium salts filtered. Concentration of the filtrates to half volume and cooling to  $-10^{\circ}\text{C}$  overnight gave complex E3 as pale yellow microcrystals (1.65 g, 71%).



Complex E3

Example 1111.1 Preparation of  $\{Cr[3,5-(CMe_3)_2-2-(O)C_6H_2CH_2NHAr]_2\}$ See Formula D2 below (Ar =  $C_6H_3-2,6-Me_2$ )

To a THF (20 ml) solution of the ligand 3,5-(CMe<sub>3</sub>)<sub>2</sub>-2-(OH)C<sub>6</sub>H<sub>2</sub>CH<sub>2</sub>NHAr (0.81 g, 2.38 mmol) was added *n*-BuLi (3.2 ml, 5.00 mmol) at -78°C. The solution was warmed to room temperature for 1 hour. On cooling, solid CrCl<sub>3</sub>(THF)<sub>3</sub> (0.90 g, 2.38 mmol) was added. The solution was warmed to room temperature and stirring continued for 12 hours. After removal of volatiles *in-vacuo*, the solid residue was extracted into pentane (50 ml). Recrystallisation from heptane afforded dark red prisms of Complex D2 on prolonged standing (1-2 days) at ambient temperature. Yield 0.62 g, (36 %).



Complex D2

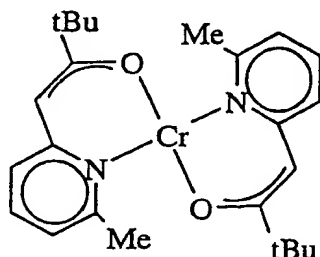
Example 1212.1 Preparation of  $\{Cr[OC(CMe_3)(=2-CHNC_5H_3Me-6)_2]\}$ See Formula E4 below

The ligand MeC(OH){2-CH<sub>2</sub>-6-Me-(C<sub>5</sub>H<sub>3</sub>N)}<sub>2</sub> (0.92 g, 3.0 mmol) and NaH (0.08 g, 3.3 mmol) in THF (30 ml) were refluxed for 12 hours. On cooling, solid CrCl<sub>2</sub>(THF)

(0.60 g, 3.0 mmol) was added and stirring continued for 12 h. After removal of volatiles *in-vacuo*, the solid residue was extracted into warm MeCN (2 x 25 ml). Blue/green prisms of Complex E4 formed on prolonged standing (1-2 days) at ambient temperature. Yield 0.48g, (37%).

5

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Complex E4

#### 15 Examples 7 to 12 - Polymerisation Tests

The Polymerisation Tests were carried out either under Schlenk-line conditions (1 bar pressure) or under higher pressure conditions (10 bar) as described below:

##### (a) Schlenk-line 1 bar Polymerisation Tests.

The chromium complex ("procatalyst") was dissolved in toluene (40 ml) in a Schlenk tube and the co-catalyst diethylaluminium chloride ("DEAC", 1.8 molar in toluene or "DMAC", 1.0 molar in toluene) was added. The Schlenk tube was then purged with ethylene and the contents magnetically stirred and maintained under ethylene (1 bar) for the duration of the polymerization. After 0.5 to 1 hour the polymerization was terminated by the addition of aqueous hydrogen chloride. The insoluble, solid, polyethylene was recovered by filtration, washed with methanol (50 ml) and dried (vacuum oven at 50 °C).

##### (b) Higher Pressure Tests.

A 1 litre reactor was baked out under a nitrogen flow for at least 1 hour at >85°C. The reactor was then cooled to 35°C. Isobutane (500ml) was then added and the reactor boxed in nitrogen and left for at least 1 hour. Ethylene was introduced into the reactor until a pre-determined over-pressure was achieved. The pre-formed catalyst solution in toluene was then injected under nitrogen. The reactor pressure was maintained constant throughout the polymerization run by computer controlled addition of ethylene. The polymerization time was 1 hour. Upon termination of the polymerisation the reactor contents were isolated, washed with aqueous HCl, methanol and dried in a vacuum oven at 50°C.

TABLE 2							
Run	Procatalyst/ (mmol)	Cocat. note 2	C <sub>2</sub> H <sub>4</sub> (bar)	Temp (°C)	Time (mins.)	Yield (g)	Activity note 1
1	D2/(0.025)	20	1	25	30	1.63	130
2	B15/(0.030)	30	1	25	60	1.48	49
3	B16a/(0.020)	30	1	25	60	1.53	122
4	B16b/(0.010)	30	1	25	60	0.79	93
5	E3/(0.020)	30	1	25	60	0.60	30
6	E3/(0.025)	25	10	35	60	30.0	120
7	D2/(0.017)	35	1	25	60	1.02	60
8	E4/(0.030)	30	1	25	60	1.21	43
9	E4/(0.030)	30	1	25	60	0.99	35

#### Notes on Table 2

Note 1 - Activity is expressed as g polymer mmol<sup>-1</sup> transition metal h<sup>-1</sup> bar<sup>-1</sup>

Note 2 - The co-catalyst quantity is expressed in equivalents. In Runs 1, 2, 3, 5, 6, 7 and 9 the cocatalyst was DEAC and in Runs 4 and 8 it was DMAC.

GPC data for Polymer samples:

Run 1: M<sub>n</sub> 84 000, M<sub>w</sub> = 827 000, M<sub>w</sub>/M<sub>n</sub> = 9.8, M<sub>pk</sub> 616 000

Run 6: M<sub>n</sub> 18 000, M<sub>w</sub> = 123 000, M<sub>w</sub>/M<sub>n</sub> = 6.9, M<sub>pk</sub> 67 000

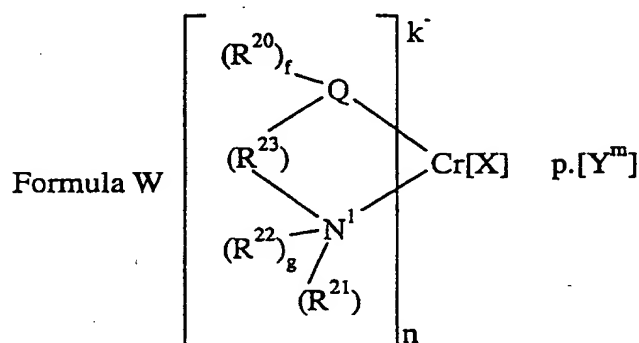
## Claims

1. A polymerisation catalyst comprising

(1) a complex chromium compound comprising the monomeric skeletal unit depicted in Formula W, or dimers of such units;

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15 having a bidentate ligand (shown in the large square brackets) wherein  $N^1$  is a nitrogen atom, Q is a nitrogen atom  $N^2$  or an oxygen atom O,  $R^{20}$  and  $R^{21}$  are organic groups;  $R^{22}$  is hydrogen or an organic group, f and g are each independently 1 or zero provided that when  $f = \text{zero}$  Q is oxygen,  $R^{23}$  is an organic group comprising at least a saturated or unsaturated chain linking  $N^1$  with

20 Q; two or more of  $R^{20}$ ,  $R^{21}$ ,  $R^{22}$  and  $R^{23}$  can optionally be linked to one another; the bonds between  $R^{23}$  and  $N^1$  or Q can be independently single or double bonds; and wherein k is the nominal negative charge on the bidentate ligand and is 1 or 2, n is the number of the defined bidentate ligands attached to the chromium atom and is 1 or 2, X is the oxidation state of the chromium and is 2 or 3, Y is an atom or a

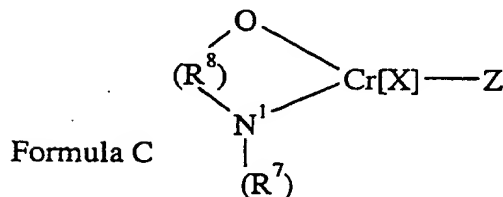
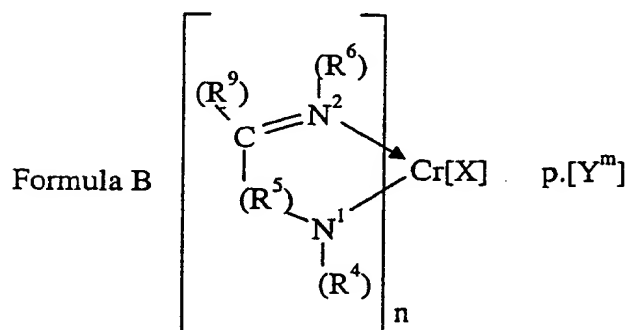
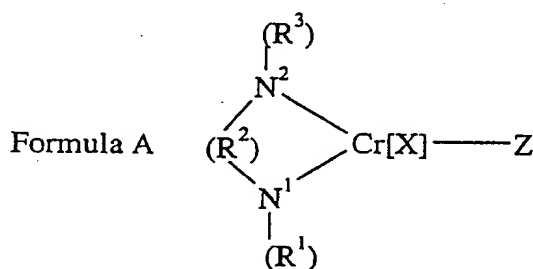
25 group having a valency of m where  $m = 1$  or 2; and p represents the number of Y atoms or groups wherein p is zero or an integer which satisfies the relationship  $p = (X - nk)/m$  and



(2) an activating quantity of an activator compound selected from organoaluminium compounds and hydrocarbylboron compounds.

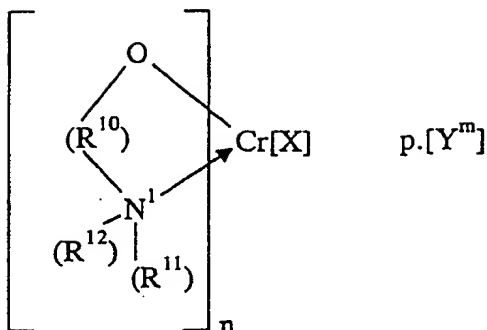
2. A catalyst as claimed in Claim 1 wherein in the chromium complex (1), in addition to the defined ligand or ligands, one or more neutral molecules are coordinated to the chromium.

3. A catalyst as claimed in Claim 1 or 2 wherein the monomeric unit of the Formula W is the monomeric unit depicted in any one of Formulae A, B, C, D, E or F:



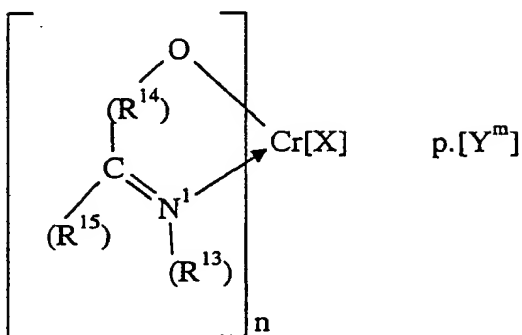
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### Formula D



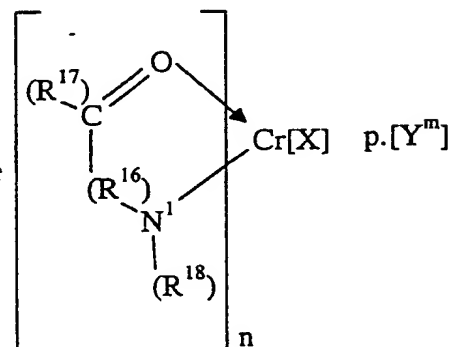
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### Formula E



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Formula F



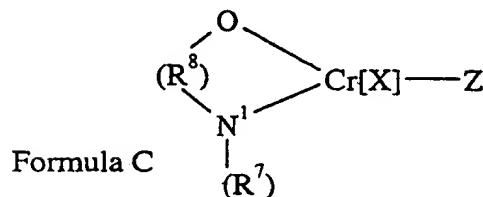
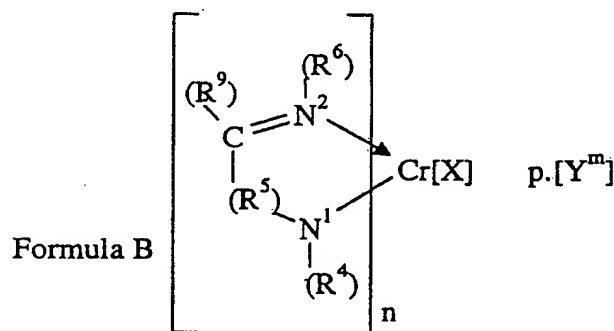
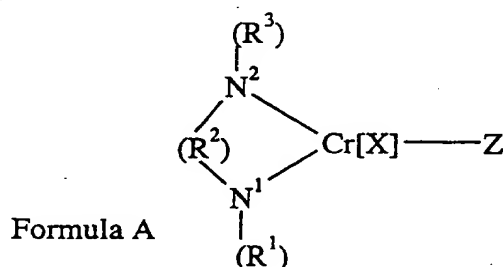
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wherein R<sup>2</sup>, R<sup>5</sup>, R<sup>8</sup>, R<sup>10</sup>, R<sup>14</sup> and R<sup>16</sup> are organic groups comprising at least a saturated or unsaturated chain; R<sup>1</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>11</sup>, R<sup>13</sup>, and R<sup>18</sup> are organic groups; R<sup>9</sup>, R<sup>12</sup>, R<sup>15</sup> and R<sup>17</sup> are independently hydrogen or organic groups; two or more of the defined R groups are optionally linked to one another within the  
35 respective Formula A, B, C, D, E, or F; N<sup>1</sup> and N<sup>2</sup> are nitrogen atoms; O is an

oxygen atom; X is the oxidation state of the chromium; in Formulae A and C, X is 3; in Formula B, D, E and F, X is 2 or 3; Z is a univalent atom or group; Y is an atom or group having a valency of m, where m = 1 or 2; p represents the number of atoms or groups of Y present in the complex unit; n is 1 or 2; and p is zero or an integer which satisfies the relationship  $p = (X-n)/m$ .

4. A catalyst as claimed in Claim 3 wherein the chromium complex of Formula A, B, C, D, E or F is in dimeric form.

5. A catalyst comprising (1) the complex chromium depicted in Formula A, B or C or dimers of such units:



- wherein  $R^2$ ,  $R^5$ , and  $R^8$  are organic bridging groups,  $R^1$ ,  $R^3$ ,  $R^4$ ,  $R^6$ , and  $R^7$  are organic groups which are optionally linked to other R group(s) within the respective Formula A, B or C;  $N^1$  and  $N^2$  are nitrogen atoms; O is an oxygen atom;  $R^9$  is hydrogen or an organic group which latter is optionally linked to other R group(s) within Formula B; X is the oxidation state of the chromium; in Formulae A and C, X is 3; in Formula B, X is 2 or 3; Z is a univalent atom or group; Y is an atom or group having a valency of m, where  $m = 1$  or  $2$ ; p represents the number of atoms or groups of Y present in the complex unit; n is 1 or 2; and p is zero or an integer which satisfies the relationship  $p = (X-n)/m$  (2) and
- (2) an activating quantity of an activator compound selected from organoaluminium compounds and hydrocarbylboron compounds.
  6. A catalyst as claimed in any one of the preceding Claims wherein  $R^1$ ,  $R^3$ ,  $R^4$ ,  $R^6$ ,  $R^7$ ,  $R^9$ ,  $R^{11}$ ,  $R^{12}$ ,  $R^{13}$ ,  $R^{15}$ ,  $R^{17}$ ,  $R^{18}$ ,  $R^{20}$ ,  $R^{21}$  and  $R^{22}$  are independently selected from methyl, ethyl, propyl, butyl, butenyl, hexyl, cyclohexyl, cyclohexenyl, octyl, benzyl, phenylethyl, phenylpropyl, phenyl, naphthyl, 2,6-dimethylphenyl, 2,4-diethylphenyl, 2,6-diisopropyl or 4-chlorophenyl.
  7. A catalyst as claimed in any one of the preceding Claims wherein  $R^{23}$ ,  $R^2$ ,  $R^5$ ,  $R^8$ ,  $R^{10}$ ,  $R^{14}$  and  $R^{16}$  are selected from organic groups comprising a saturated chain linking  $N^1$  with  $N^2$  or O.
  8. A catalyst as claimed in any one of Claims 1 to 6 wherein  $R^{23}$ ,  $R^2$ ,  $R^5$ ,  $R^8$ ,  $R^{10}$ ,  $R^{14}$  and  $R^{16}$  are selected from organic groups comprising an unsaturated chain linking  $N^1$  with  $N^2$  or O.
  9. A catalyst as claimed in Claim 8 wherein the unsaturated chain comprises or forms part of an aromatic ring system or a system of conjugated double bonds.
  10. A catalyst as claimed in any one of the preceding Claims wherein Y is selected from halide, sulphate, nitrate, thiolate, thiocarboxylate,  $BF_4^-$ ,  $PF_6^-$ , hydride, hydrocarbyloxy, carboxylate, hydrocarbyl, substituted hydrocarbyl, and heterohydrocarbyl.
  11. A catalyst as claimed in any one of the preceding Claims wherein the activator compound is selected from trimethylaluminium, triethylaluminium, tributylaluminium, tri-n-octylaluminium, ethylaluminium dichloride, diethylaluminium chloride and alumoxanes.
  12. A catalyst as claimed in any one of the preceding Claims and supported on a support material.
  13. A catalyst as claimed in Claim 12 wherein the support material is silica or

alumina.

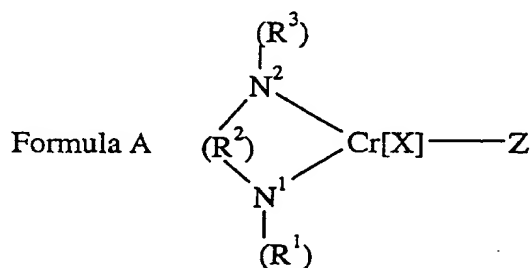
14. A process for polymerisation or copolymerisation of 1-olefins comprising contacting the monomeric 1-olefin under polymerisation conditions with the catalyst claimed in any one of the preceding Claims.

5 15. A process as claimed in Claim 14 wherein one or more monomers selected from ethylene, propylene, 1-butene, 1-hexene, 4-methylpentene-1, and octene are polymerised or copolymerised.

16. A process as claimed in Claim 14 or 15 wherein the polymerisation conditions are such that the polymer forms as particles in an inert liquid diluent.

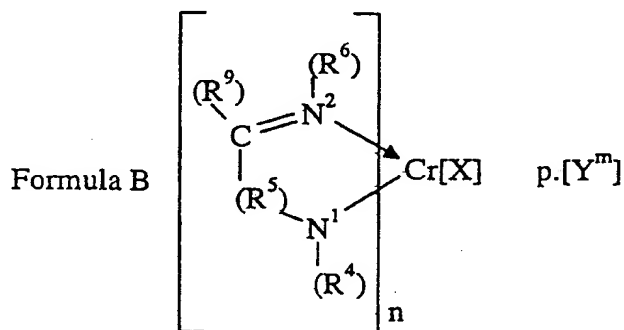
10 18 A process as claimed in Claim 14 or 15 wherein the polymerisation conditions are gas phase fluidised bed.

19 A complex chromium compound having the Formula A, or a dimer thereof:



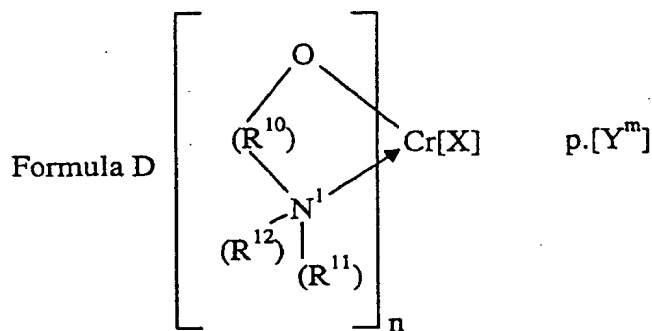
20 wherein  $\text{R}^2$ , is an organic group comprising at least a saturated or unsaturated chain;  $\text{R}^1$  and  $\text{R}^3$  are organic groups; two or more of the defined R groups are optionally linked to one another;  $\text{N}^1$  and  $\text{N}^2$  are nitrogen atoms; X is the oxidation state of the chromium; Z is a univalent atom or group.

25 20. A complex chromium compound having the Formula B, or a dimer thereof:



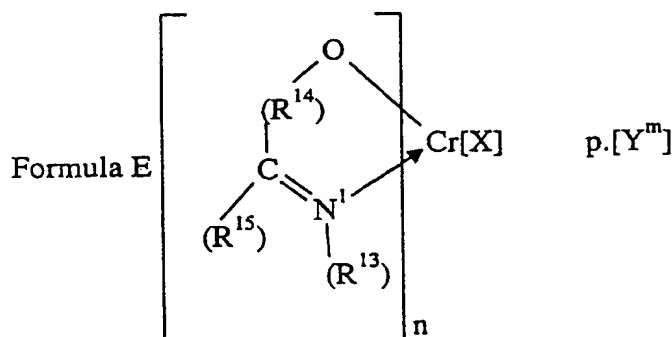
wherein  $R^5$  is an organic group comprising at least a saturated or unsaturated chain;  $R^4$  and  $R^6$  are organic groups;  $R^9$  is hydrogen or an organic groups; two or more of the defined R groups are optionally linked to one another;  $N^1$  and  $N^2$  are nitrogen atoms; X is the oxidation state of the chromium and is 3; Y is an atom or group having a valency of m, where  $m = 1$  or  $2$ ; p represents the number of atoms or groups of Y present in the complex unit; n is 1 or 2; and p is zero or an integer which satisfies the relationship  $p = (X-n)/m$ .

21. A complex chromium compound having the Formula D, or a dimer thereof:



wherein  $R^{10}$  is an organic group comprising at least a saturated or unsaturated chain;  $R^{11}$  is an organic group;  $R^{12}$  is independently hydrogen or an organic group; two or more of the defined R groups are optionally linked to one another;  $N^1$  is a nitrogen atom; O is an oxygen atom; X is the oxidation state of the chromium and is 2; Y is an atom or group having a valency of m, where  $m = 1$  or  $2$ ; p represents the number of atoms or groups of Y present in the complex unit; n is 1 or 2; and p is zero or an integer which satisfies the relationship  $p = (X-n)/m$ .

22. A complex chromium compound having the Formula E, or a dimer thereof:



wherein  $R^{14}$  is an organic group comprising at least a saturated or unsaturated chain;  
 $R^{13}$  is an organic group;  $R^{15}$  is hydrogen or an organic group; two or more of the  
defined R groups are optionally linked to one another;  $N^1$  is a nitrogen atom; O is an  
oxygen atom; X is the oxidation state of the chromium and is 2; Y is an atom or group  
5 having a valency of m, where  $m = 1$  or  $2$ ; p represents the number of atoms or groups  
of Y present in the complex unit; n is 1 or 2; and p is zero or an integer which  
satisfies the relationship  $p = (X-n)/m$ .

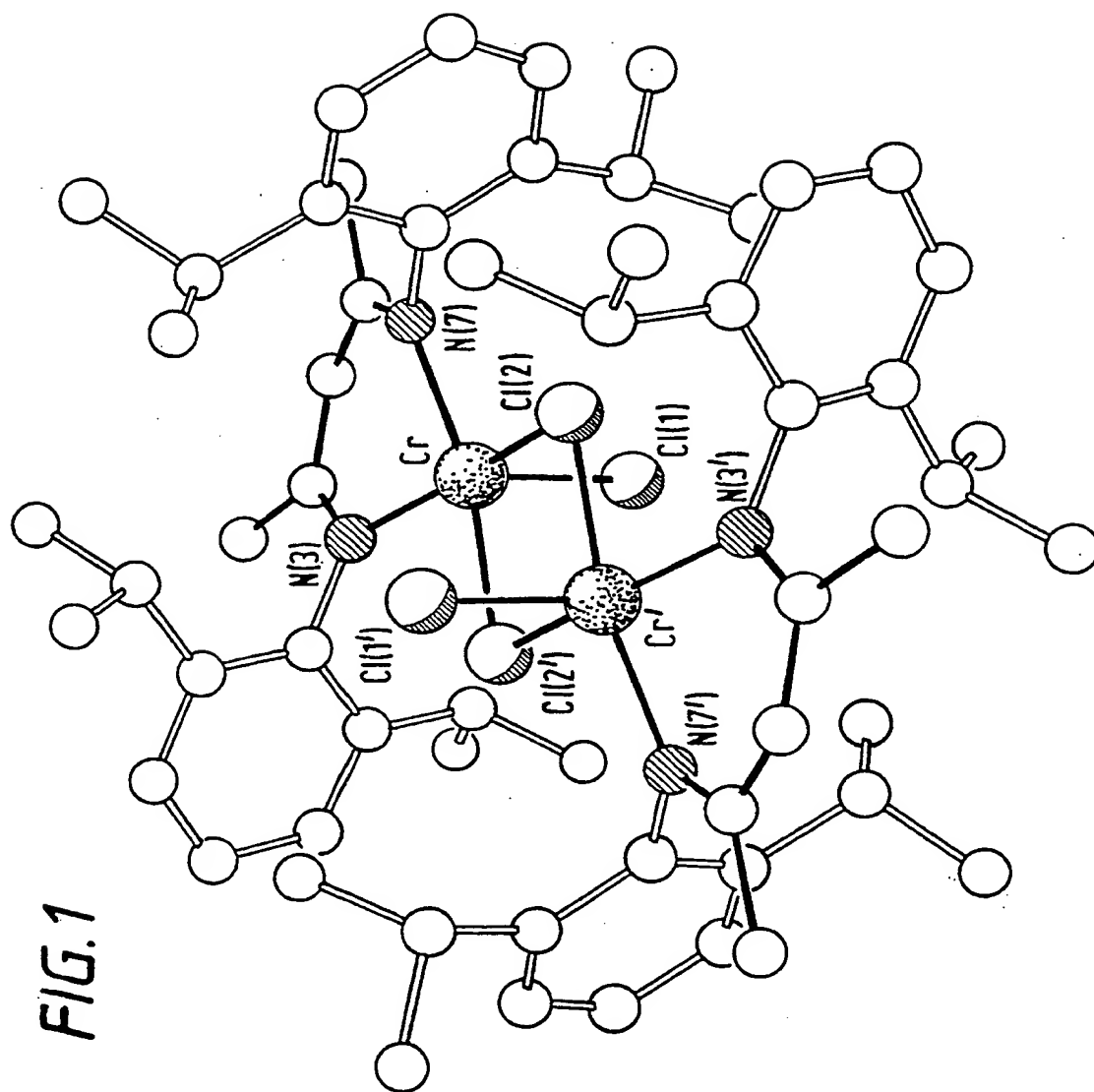
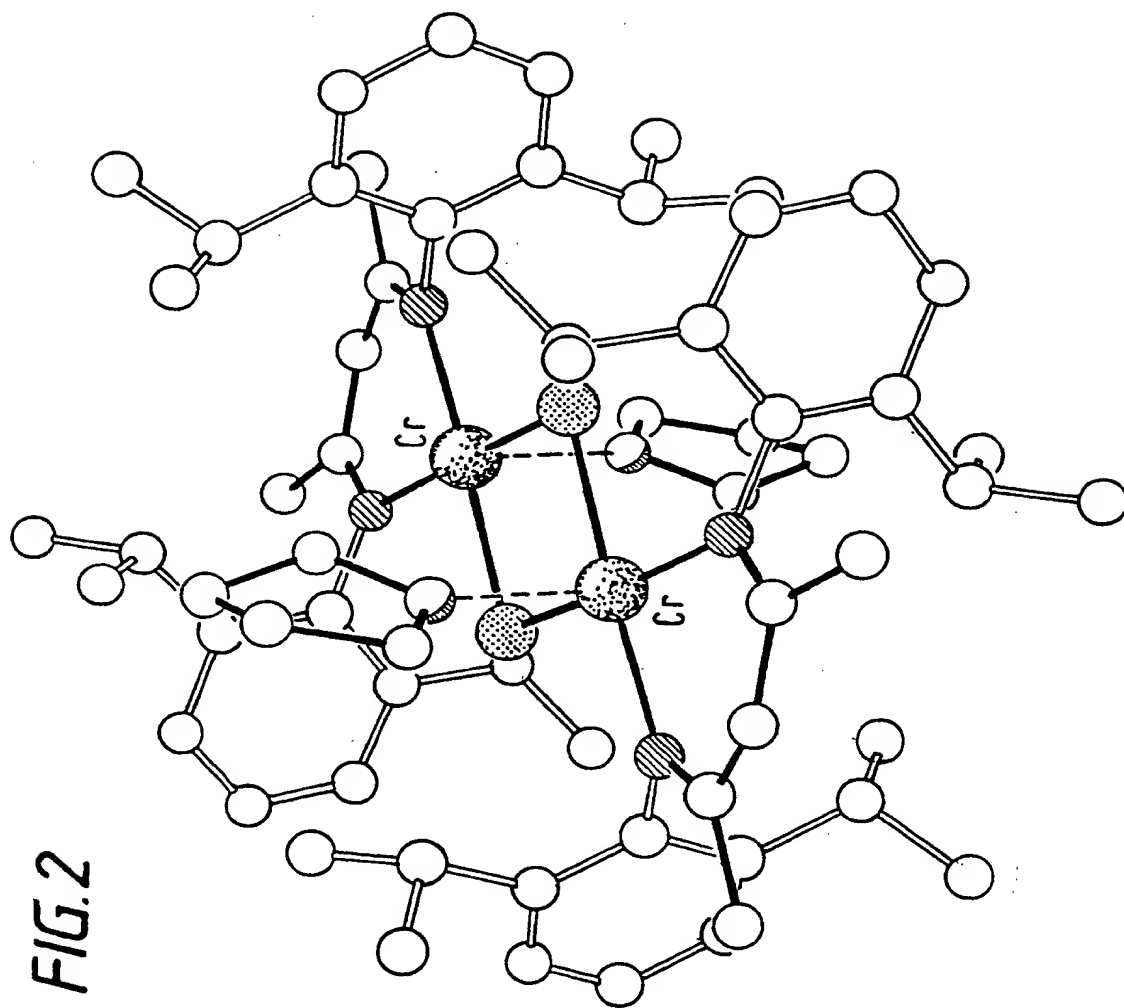
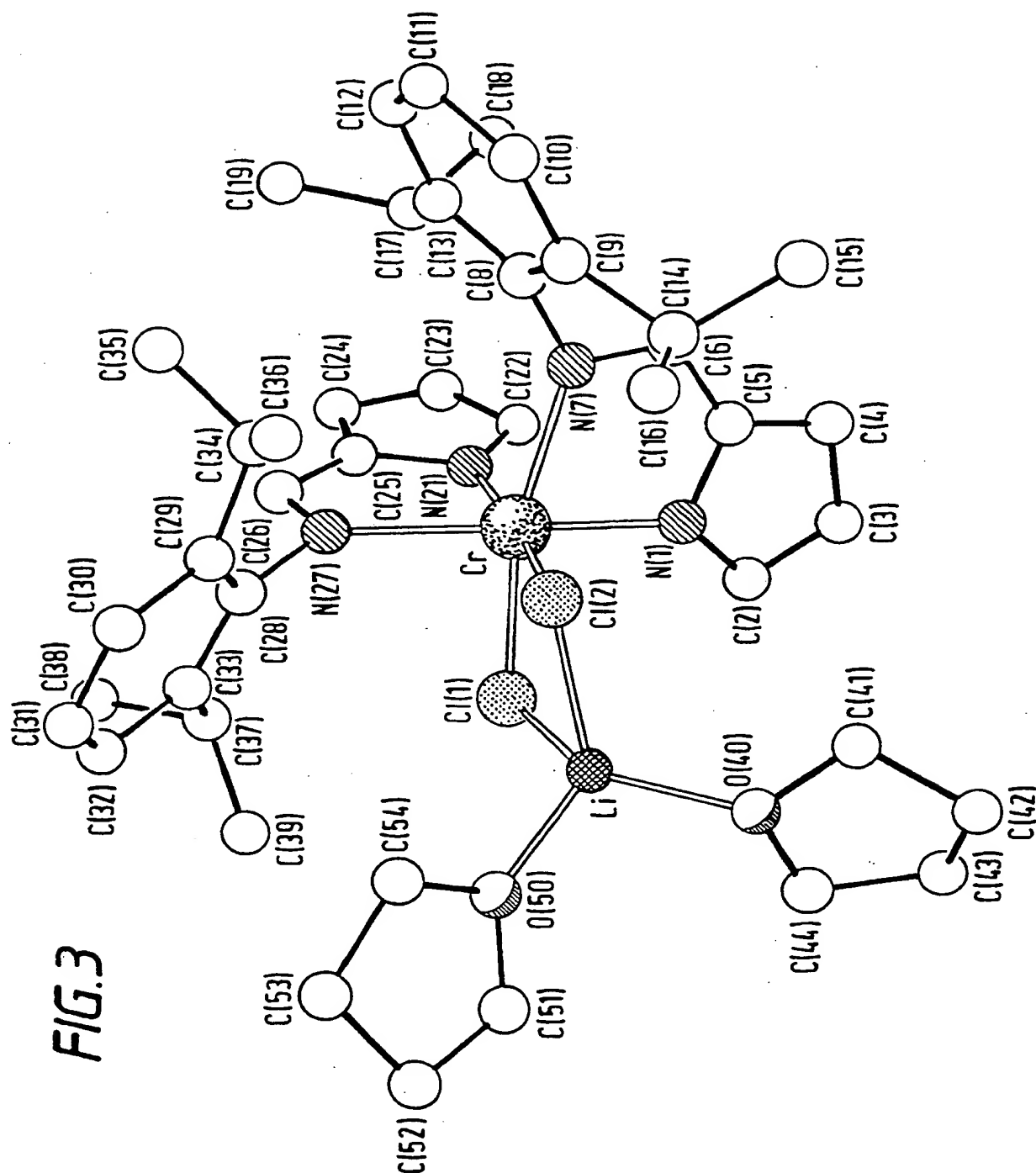


FIG.1







# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/03027

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07F11/00 C08F4/69 C08F10/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07F C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	<p>GIBSON, VERNON C. ET AL: "Chromium(III) complexes bearing N,N-chelate ligands as ethene polymerization catalysts"</p> <p>CHEM. COMMUN. (CAMBRIDGE) (1998), (16), 1651-1652 CODEN: CHCOFS; ISSN: 1359-7345, XP002089037</p> <p>see page 1651, column 2, paragraph 2</p> <p>see scheme 1, complex 4</p> <p>see examples 10-12; table 1</p> <p style="text-align: center;">---</p> <p style="text-align: center;">-/--</p>	<p>1, 3-11, 14, 15, 20</p>

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search

8 January 1999

Date of mailing of the international search report

25/01/1999

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## INTERNATIONAL SEARCH REPORT

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PCT/GB 98/03027

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X	HANSEN, C.B. ET AL: "Metalloporphyrins as catalysts in the decomposition of cyclohexyl hydroperoxide" CATAL. LETT. (1993), 20(3-4), 359-64 CODEN: CALEER; ISSN: 1011-372X, XP002089040 see abstract see example 4; table 1	20
X	HABER, J. ET AL: "Oxidation of cyclohexane with hydrogen peroxide and chlorotetratolylporphyrinatochromium(III) as catalyst" J. MOL. CATAL. (1989), 55(1-3), 268-75 CODEN: JMCADS; ISSN: 0304-5102, XP002089041 see the whole document	20
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International Application No

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A	WO 96 24601 A (UNIV DUBLIN ;DECLAN GILHEANY (IE); RYAN KENNETH (IE); DALTON CORMA) 15 August 1996 see page 28 ----	22
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E	EP 0 874 005 A (MITSUI CHEMICALS INC) 28 October 1998  see claims 1,12 -----	1,3-5, 8-11,14, 15

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Information on patent family members

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